

**KINETICS AND MECHANISMS OF THE REDOX REACTIONS OF CRYSTAL  
VIOLET WITH SOME OXYANIONS IN AQUEOUS ACIDIC MEDIUM**

**BY**

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**JUNE, 2015**

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VIOLET WITH SOME OXYANIONS IN AQUEOUS ACIDIC MEDIUM**

**BY**

**Safiya ABDULSALAM, B.TECH Industrial Chemistry (ATBU) 2011  
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**DEPARTMENT OF CHEMISTRY  
FACULTY OF SCIENCE  
AHMADU BELLO UNIVERSITY, ZARIA  
NIGERIA**

**JUNE, 2015**

## DECLARATION

I declare that the work in this thesis entitled □ □Kinetics and mechanisms of the redox reactions of crystal violet with some oxyanions in aqueous acidic medium□ has been carried out by me in the Department of Chemistry of Ahmadu Bello University Zaria under the supervision of Dr. S. O. Idris and Prof. J.F. Iyun (Late). To the best of my knowledge, no part of this work was previously presented for the award of another degree and/or diploma by me or anyone else at this or any other institution. All information obtained from literature has been duly acknowledged in the text and a list of references provided.

Safiya ABDULSALAM

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

## CERTIFICATION

This thesis entitled: □ □ Kinetics and mechanisms of the redox reactions of crystal violet with some oxyanions in aqueous acidic medium □ by Safiya ABDULSALAM, meets the regulations governing the award of the degree of Master of Science in Inorganic Chemistry of Ahmadu Bello University Zaria, and is approved for its contribution to knowledge and literary presentation.

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## ACKNOWLEDGMENT

All praises and gratitude are due to Almighty Allah, The All and All, The Being, The Been and The to Be, Allah of mercies, your unquantifiable love is overwhelming. May the peace and blessings of Allah continue to cascade upon the noble Prophet Muhammad (SAW), his household, his companions and all who follow them till the day of reckoning! Amin.

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Finally, I would like to specially appreciate my beloved parents for their support, spiritually and morally, may Allah reserve the highest palace for you in Jannah! Amin.

## **DEDICATION**

This work is dedicated to my beloved parents, Alhaji Mustapha Abdulsalam and Hajiya Maimunat Badamasi.

## ABSTRACT

The kinetics and mechanisms of the redox reaction of crystal violet (hereafter CV<sup>+</sup>) was studied with some oxyanions (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>, BrO<sub>3</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup> and ClO<sup>-</sup>) in aqueous acidic medium. The stoichiometries of the reactions were found to be 1:1 for CV<sup>+</sup>- S<sub>2</sub>O<sub>5</sub><sup>2-</sup>, 2:3 for CV<sup>+</sup>- BrO<sub>3</sub><sup>-</sup>, and 1:2 for CV<sup>+</sup>- IO<sub>4</sub><sup>-</sup> and CV<sup>+</sup>- ClO<sup>-</sup> systems. The order of the reactions was one with respect to both oxidant and reductant in CV<sup>+</sup>- S<sub>2</sub>O<sub>5</sub><sup>2-</sup>, -BrO<sub>3</sub><sup>-</sup> and -ClO<sup>-</sup> reactions respectively. For the CV<sup>+</sup>- IO<sub>4</sub><sup>-</sup> system, the order of the reaction was one with respect to the [CV<sup>+</sup>] and zero with respect to [IO<sub>4</sub><sup>-</sup>]. Studies on the influence of [H<sup>+</sup>] on the rates of reactions point to two parallel pathways for S<sub>2</sub>O<sub>5</sub><sup>2-</sup>, BrO<sub>3</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup> reactions and one reaction pathway for ClO<sup>-</sup> reaction. The reaction conformed to the following rate equations:

$$\frac{-d[CV^+]}{dt} = (a + b [H^+]^{-1})[CV^+][S_2O_5^{2-}]$$

$$a = 2.27 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } b = 0.86 \text{ s}^{-1}$$

$$\frac{-d[CV^+]}{dt} = (c + d [H^+]^2)[CV^+][BrO_3^-]$$

$$c = 9.22 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } d = 1.16 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$$

$$\frac{-d[CV^+]}{dt} = (e + f [H^+])[CV^+]$$

$$e = 1.49 \text{ s}^{-1} \text{ and } f = 1.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\frac{-d[CV^+]}{dt} = (g [H^+])[CV^+][ClO^-]$$

$$g = 6.16 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

the rate of the reaction displayed positive salt effect for CV<sup>+</sup>- BrO<sub>3</sub><sup>-</sup> and CV<sup>+</sup>- IO<sub>4</sub><sup>-</sup> reactions and negative salt effect was observed for CV<sup>+</sup>- S<sub>2</sub>O<sub>5</sub><sup>2-</sup> reaction. In the case of CV<sup>+</sup>- ClO<sup>-</sup> reaction, increase in ionic strength has no effect on the rate of reaction. Added anions inhibited the rate of reactions of CV<sup>+</sup>- S<sub>2</sub>O<sub>5</sub><sup>2-</sup> and CV<sup>+</sup>- BrO<sub>3</sub><sup>-</sup> but increased that of CV<sup>+</sup>- ClO<sup>-</sup>, while added anions has no effect on the rate of reaction for CV<sup>+</sup>- IO<sub>4</sub><sup>-</sup>. Added cations had no effect on the rate of reactions of all the systems except for CV<sup>+</sup>- BrO<sub>3</sub><sup>-</sup> where the rate of the reaction decreased with increase in cation concentration. Spectroscopic investigations and Michaelis-Menten plot showed no evidence of intermediate complex formation in all the reactions except for CV<sup>+</sup>- IO<sub>4</sub><sup>-</sup> where evidence of intermediate complex was noticed by shift in λ<sub>max</sub> from 585 to 620 nm. Outersphere mechanism was proposed for all the systems except CV<sup>+</sup>- IO<sub>4</sub><sup>-</sup> system where the reaction was believed to proceed via innersphere mechanism.

## TABLE OF CONTENTS

Contents	Page
Cover page	i
Title page	ii
Declaration	iii
Certification	iv
Acknowledgement	v
Dedication	vi
Abstract	vii
Table of Content	viii
List of Tables	xii
List of Figures	xiii
Abbreviations	xvi
<b>CHAPTER ONE</b>	
<b>1.0 INTRODUCTION</b>	<b>1</b>
<b>1.1 Kinetic studies</b>	<b>2</b>
<b>1.2 Electron transfer reactions</b>	<b>2</b>
<b>1.3 Oxidation-reduction in inorganic reactions</b>	<b>3</b>
<b>1.4 Outersphere mechanism</b>	<b>3</b>
1.4.1 Consideration for outersphere mechanism	4
<b>1.5 Innersphere mechanism</b>	<b>4</b>
1.5.1 Consideration for innersphere mechanisms	5
<b>1.6 Probable ways of electron transfer reactions</b>	<b>5</b>
1.6.1 Complimentary reactions	5
1.6.2 Non-complimentary reactions	6



<b>1.7 Justification</b>	<b>6</b>
<b>1.8 Aim</b>	<b>8</b>
<b>1.9 Objectives</b>	<b>8</b>
<b>CHAPTER TWO</b>	
<b>2.0 LITERATURE REVIEW</b>	<b>9</b>
<b>2.1 Reactions of crystal violet</b>	<b>9</b>
<b>2.2 Reactions of metabisulphite ion</b>	<b>11</b>
<b>2.3 Reactions of periodate ion</b>	<b>13</b>
<b>2.4 Reactions of bromate ion</b>	<b>16</b>
<b>2.5 Reactions of hypochlorite ion</b>	<b>18</b>
<b>CHAPTER THREE</b>	
<b>3.0 MATERIALS AND METHODS</b>	<b>20</b>
<b>3.1 Materials</b>	<b>20</b>
3.1.1 Crystal violet	20
3.1.2 Preparation of sodium metabisulphite solution	21
3.1.3 Preparation of potassium bromate solution	21
3.1.4 Preparation of sodium periodate solution	21
3.1.5 Preparation of sodium hypochlorite solution	21
3.1.6 Preparation of standard solution of hydrochloric acid	21
3.1.7 Preparation of $0.1 \text{ mol dm}^{-3} \text{ Na}_2 \text{ B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$ (Borax)	22
3.1.8 Preparation of standard solution of perchloric acid	22
3.1.9 Preparation of standard sodium perchlorate solution	22
3.1.10 Preparation of standard sodium chloride solution	22
3.1.11 Preparation of sodium carbonate solution	22
3.1.12 Preparation of salt solutions	23

<b>3.2</b>	<b>Methods</b>	<b>23</b>
3.2.1	Stoichiometric studies	23
3.2.2	Kinetic measurements	23
3.2.3	Effect of $[H^+]$ on the reaction rate	25
3.2.4	Effect of ionic strength and dielectric constant of the reaction medium on the reaction rate	25
3.2.5	Effect of added ions on the reaction rate	26
3.2.6	Test for intermediate complex	26
3.2.7	Test for free radicals	26
3.2.8	Product analyses	27
<b>CHAPTER FOUR</b>		
<b>4.0</b>	<b>RESULTS</b>	<b>28</b>
<b>4.1</b>	<b>Stoichiometry</b>	<b>28</b>
<b>4.2</b>	<b>Determination of order of the reactions with respect to the reactants</b>	<b>29</b>
<b>4.3</b>	<b>Effect of hydrogen ion concentration on the rates of the reactions.</b>	<b>49</b>
<b>4.4</b>	<b>The effect of ionic strength of the reaction medium on the reaction rate</b>	<b>58</b>
<b>4.5</b>	<b>The effect of changes in dielectric constant of the reaction medium on the reaction rate</b>	<b>62</b>
<b>4.6</b>	<b>Effect of added ions on the reaction rate</b>	<b>62</b>
<b>4.7</b>	<b>Test for intermediate complex</b>	<b>79</b>
4.7.1	Test for free radicals	79
4.7.2	Michaelis-Menten plot	79
4.7.3	Spectrophotometric test	79
<b>4.8</b>	<b>Products analyses</b>	<b>89</b>
<b>CHAPTER FIVE</b>		
<b>5.0</b>	<b>DISCUSSION</b>	<b>90</b>

<b>5.1 Crystal violet- metabisulphite ion system</b>	<b>90</b>
<b>5.2 Crystal violet-bromate ion system.</b>	<b>93</b>
<b>5.3 Crystal violet- hypochlorite ion system</b>	<b>97</b>
<b>5.4 Crystal violet-periodate ion system</b>	<b>99</b>
<b>CHAPTER SIX</b>	
<b>6.0 SUMMARY, CONCLUSION AND RECOMMENDATION</b>	<b>104</b>
<b>6.1 Summary</b>	<b>104</b>
<b>6.2 Conclusion</b>	<b>105</b>
<b>6.3 Recommendation</b>	<b>106</b>
<b>References</b>	<b>107</b>

## LIST OF TABLES

4.1	Pseudo-first order and second order rate constants for the redox reaction of crystal violet with metabisulphite ions	38
4.2	Pseudo-first order and second order rate constants for the redox reaction of crystal violet with bromate ions	39
4.3	Pseudo-first order and second order rate constants for the redox reaction of crystal violet with hypochlorite ions	40
4.4	Pseudo-first order rate constants for the redox reaction of crystal violet with periodate ions	41
4.5	Pseudo-first order and second order rate constants for the effect of change in dielectric constant of the medium on the redox reaction of crystal violet with bromate ion	63
4.6	Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of crystal violet with metabisulphite ion	65
4.7	Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of crystal violet with bromate ion	66
4.8	Pseudo-first order rate constants for the effect of added anions on the redox reaction of crystal violet with periodate ion	67
4.9	Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of crystal violet with hypochlorite ion	68
4.10	Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with metabisulphite ion	75
4.11	Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with bromate ion	76
4.12	Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with periodate ion	77
4.13	Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with hypochlorite ion	78

## LIST OF FIGURES

4.1	Plot of absorbance versus mole ratio for the redox reaction of crystal violet with metabisulphite ion	30
4.2	Plot of absorbance versus mole ratio for the redox reaction of crystal violet with bromate ion	31
4.3	Plot of absorbance versus mole ratio for the redox reaction of crystal violet with periodate ion	32
4.4	Plot of absorbance versus mole ratio for the redox reaction of crystal violet with hypochlorite ion	33
4.5	Typical pseudo-first order plot for the redox reaction of crystal violet with metabisulphite ions	34
4.6	Typical pseudo-first order plot for the redox reaction of crystal violet with bromate ions	35
4.7	Typical pseudo-first order plot for the redox reaction of crystal violet with periodate ions	36
4.8	Typical pseudo-first order plot for the redox reaction of crystal violet with hypochlorite ions	37
4.9	Plot of $k_1$ versus $[S_2O_5^{2-}]$ for the reaction of crystal violet and metabisulphite ion	42
4.10	Plot of $k_1$ versus $[BrO_3^-]$ for the reaction of crystal violet and bromate ion	43
4.11	Plot of $k_1$ versus $[ClO^-]$ for the reaction of crystal violet and hypochlorite ion	44
4.12	Pseudo-first order plot of $\log k_1$ versus $\log [S_2O_5^{2-}]$ for the redox reaction of crystal violet with metabisulphite ions	46
4.13	Pseudo-first order plot of $\log k_1$ versus $\log [BrO_3^-]$ for the redox reaction of crystal violet with bromate ions	47
4.14	Pseudo-first order plot of $\log k_1$ versus $\log [ClO^-]$ for the redox reaction of crystal violet with hypochlorite ions	48

4.15	Plot of $\log k_1$ versus $\log [H^+]$ for the redox reaction of crystal violet with metabisulphite ion	50
4.16	Plot of $\log k_1$ versus $\log [H^+]$ for the redox reaction of crystal violet with bromate ion	51
4.17	Plot of $\log k_1$ versus $\log [H^+]$ for the redox reaction of crystal violet with periodate ion	52
4.18	Plot of $\log k_1$ versus $\log [H^+]$ for the redox reaction of crystal violet with hypochlorite ion	53
4.19	Plot of $k_2$ versus $1/[H^+]$ for the redox reaction of crystal violet with metabisulphite ion	54
4.20	Plot of $k_2$ versus $[H^+]^2$ for the redox reaction of crystal violet with bromate ion	55
4.21:	Plot of $k_2$ versus $[H^+]$ for the redox reaction of crystal violet with periodate ion	56
4.22	Plot of $k_2$ versus $[H^+]$ for the redox reaction of crystal violet with hypochlorite ion	57
4.23	Plot of $\log k_2$ versus $\sqrt{I}$ for the redox reaction of crystal violet with metabisulphite ion	59
4.24	Plot of $k_2$ versus $\sqrt{I}$ for the redox reaction of crystal violet with bromate ion	60
4.25	Plot of $k_1$ versus $\sqrt{I}$ for the redox reaction of crystal violet with periodate ion	61
4.26	Plot of $k_2$ against $1/D$ for the redox reaction of crystal violet with bromate ion	64
4.27	Plot of $k_2$ versus $[SO_4^{2-}]$ for the redox reaction crystal violet with metabisulphite ion	69
4.28	Plot of $k_2$ versus $[CH_3COO^-]$ for the redox reaction crystal violet with metabisulphite ion	70
4.29	Plot of $k_2$ versus $[SO_4^{2-}]$ for the redox reaction crystal violet with bromate ion	71
4.30	Plot of $k_2$ versus $[CH_3COO^-]$ for the redox reaction crystal violet with bromate ion	72

4.31	Plot of $k_2$ versus $[\text{SO}_4^{2-}]$ for the redox reaction crystal violet with hypochlorite ion	73
4.32	Plot of $k_2$ versus $[\text{CH}_3\text{COO}^-]$ for the redox reaction crystal violet with hypochlorite ion	74
4.33	Plot of $k_2$ versus $[\text{Ca}^{2+}]$ for the redox reaction crystal violet with bromate ion	80
4.34	Plot of $k_2$ versus $[\text{Mg}^{2+}]$ for the redox reaction crystal violet with bromate ion	81
4.35	Michaelis-Menten plot of $1/k_1$ versus $1/[\text{S}_2\text{O}_5^{2-}]$ for the redox reaction of crystal violet with metabisulphite ion	82
4.36	Michaelis-Menten plot of $1/k_1$ versus $1/[\text{BrO}_3^-]$ for the redox reaction of crystal violet with bromate ion	83
4.37	Michaelis-Menten plot of $1/k_1$ versus $1/[\text{ClO}^-]$ for the redox reaction of crystal violet with hypochlorite ion	84
4.38	Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and metabisulphite ion	85
4.39	Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and bromate ion	86
4.40	Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and hypochlorite ion	87
4.41	Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and periodate ion	88

## ABBREVIATIONS

ABBREVIATION	NAME
abs	Absorbance
aq	Aqueous
BDH	British Drug House
Cald	Calculated
CV <sup>+</sup>	Crystal violet
Eq	Equation
k	Rate constant
K	Equilibrium constant
M & B	May and Baker
NMR	Nuclear Magnetic Resonance
Obsd	Observed
Ox	Oxidant
Red	Reductant
Sub	Substitution
$\lambda_{\max}$	Wavelength of maximum absorption
EDTA	Ethylenediaminetetraacetate
EDDA	Ethylenediaminediacetate
HEDTA	N-2-hydroxyethylethylenediaminetriacetate
D	Dielectric constant
TLC	Thin Layer Chromatography



## CHAPTER ONE

### 1.0 INTRODUCTION

Inorganic chemistry is concerned with the properties and behaviour of inorganic compounds, which include metals, minerals and organometallic compounds. Areas of research interest in inorganic chemistry include organometallic chemistry with bias toward catalysis, coordination chemistry and the biochemical role of metals (Purcell and Kotz, 1977). In all these areas of interest, the focus has been on reaction kinetics especially electron transfer or redox reactions. Knowledge of these reactions constitutes an inevitable pre-requisite to the understanding, development and eventual effective control of a wide area of science and technology (Iyun, 1982).

Reactions of metal ion complexes often involve ligand substitution or electron transfer or both. Electron transfer (ET) is one of many pathways by which redox reaction can occur, and this is thought to provide a low energy pathway for redox reaction. A typical example is the oxidation of both metal ions and non-metallic substrate by chromium(VI) ion (Beagle and Height, 1972).

In redox reactions, the stability and reactivity of an ion in any oxidation state is greatly influenced by the presence of ligands. A particular oxidation state may be said to be stable only when its redox reactions involve an unfavourable free energy change or the activation energies for the intramolecular electron transfer processes are too large (Sutin, 1968; Taube, 1968; Chaffee and Edwards, 1970). When these two factors are favourable, a redox process is spontaneous and it is often accompanied by changes in the oxidation state of at least two of the

reactants. The investigation of the mechanism of a large number of these electron transfer reactions has been reported (Sutin 1962, Sykes, 1966; Wilkins, 1974, Burgess, 1978).

### **1.1 Kinetic studies**

Chemical kinetics deals with the rates of chemical reactions and the factors affecting rates of reaction. Kinetics study is important in providing essential evidence as to the mechanisms of chemical processes. In chemical reactions, there are two basic questions that must be answered; does the reaction want to go? This has to do with chemical thermodynamics and if the reaction wants to go, how fast will it go? This has to do with chemical kinetics (Zuckerman, 1986).

### **1.2 Electron transfer reactions**

Electron transfer reactions play a central role in physical, chemical and biological processes. Because of the ubiquity of electron transfer processes, the study of electron transfer reactions, perhaps more so than that of any other area of chemistry is characterized by a strong interplay of theory and experiment (Zuckerman, 1986), nonetheless the importance of electron transfer in transition metal redox chemistry has been recognized (Wilkinson, 1987).

The work of Taube (1967) in redox systems unequivocally demonstrated the transport of electron from reductant to oxidant. This discovery certainly added many important features in the syntheses of coordination complexes and organometallics. It is such a subject, which has manifestations in almost all walks of life. Oxidation-reduction reaction needs at least two reactants, one capable of gaining electrons (oxidant) and the other capable of losing electrons

(reductant). Redox reactions are the basis for numerous biochemical pathways and cellular chemistry, biosynthesis, and regulation (Shapiro, 1972).

### 1.3 Oxidation-reduction in inorganic reactions

Oxidation-reduction reaction may involve one or more electron transfers. Depending upon the number of electrons transferred between oxidant and reductant, the reaction may proceed in one or more steps. Electron transfer reactions may occur by either of two mechanisms: outersphere mechanisms and innersphere mechanisms (Banerjee, 1993).

#### 1.4 Outersphere mechanism

In this mechanism, the coordination shells of the complexes or metal ion remains intact, during the course of electron transfer. Outersphere electron transfer is generally enthalpically less favorable than innersphere electron transfer because the interaction through space between the redox centers in outersphere electron transfer is weaker than the interaction through the chemical bridge present in the innersphere mechanism. By the same token, outersphere electron transfer is usually entropically more favorable than innersphere electron transfer as the two sites involved do not have to go through the ordering processes associated with the formation of a bridge (Mcnaught and Wilkinson, 1997). Such a mechanism is established when rapid electron transfer occurs between two substitution-inert complexes.

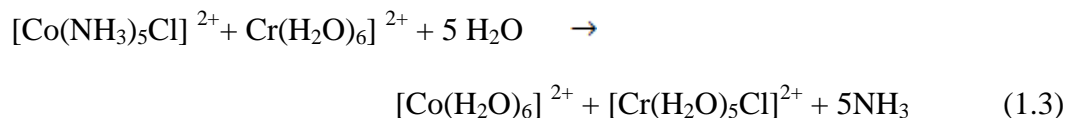


#### 1.4.1 Considerations for outersphere mechanisms

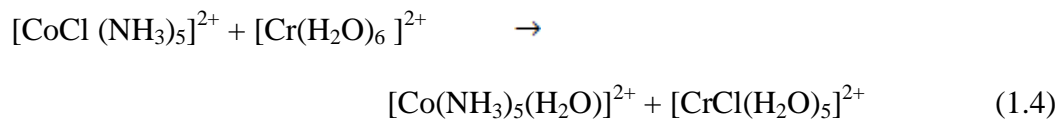
The reactants in an outersphere mechanism must get close together for tunneling to occur, bond lengthening and shortening must occur and Franck-Condon principle must be obeyed such that electronic transitions (and electron transfer) occur on a far shorter time scale than molecular vibrations (nuclear motion). This means that electron transfer will only occur when the reactants are distorted to the appropriate geometry for the products, that is, this imposes an electronic barrier on the rate of electron transfer (Mcnaught and Wilkinson, 1997).

#### 1.5 Innersphere mechanism

An innersphere mechanism is one in which the reactant and oxidant share a ligand transitorily in their inner or primary co-ordination spheres forming a bridged intermediate activated complex. The discoverer of the innersphere mechanism was Henry Taube (Taube, 1967), who was awarded the Nobel Prize in Chemistry in 1983 for these pioneering studies. A particularly historic finding is summarized below:



The electron being transferred across a bridging group. An example is given below



### 1.5.1 Considerations for innersphere mechanisms

The innersphere mechanisms normally obey three distinct steps; substitution to form a bridge between oxidant and reductant, actual electron transfer and separation of the products often with transfer of the bridging ligand (Taube and Meyers, 1953).

## 1.6 Probable ways of electron transfer reactions

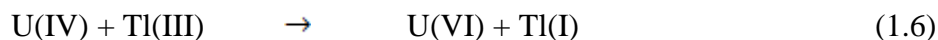
Complementary and Non-complementary reactions are types of electron transfer reactions as depicted by Basolo and Pearson (1967) and Sharma *et al.*, (1988).

### 1.6.1 Complementary reactions

The oxidant and reductant change their oxidation state by an equal number of units. These are termed as complementary electron transfer reactions (Malik *et al.*, 1996). Complementary reaction can be explained in term of; one equivalent–one equivalent reaction, in which there occurs the transfer of one electron from one species to the other. These simple reactions serve as models for more complicated systems and their study has proved invaluable in developing and understanding of the electron transfer in solution (Taube, 1959).



Two-equivalent–two-equivalent reactions in which there occurs the transfer of two electrons from one species to the other (Taube, 1957; Harkness and Halpern, 1959):



A large number of complementary reactions have been explained by assuming the formation of bridged activated complexes between the oxidant and the reductant for the facile transfer of electron through the bridging ligand.

### 1.6.2 Non-complementary reactions

The oxidant and the reductant change their oxidation states by a different number of units. These are termed as non-complementary electron transfer reactions (Wiberg, 1965). Most of the non-complementary reactions proceed via elementary steps each involving one electron transfers. The most commonly observed kinetic scheme as illustrated by Wiberg, (1965) is shown below.



### 1.7 Justification

Crystal violet or Gentian violet (also known as hexamethyl pararosaniline chloride) is a triphenylmethane dye that is useful in multiple areas of human endeavour. In medicine, crystal violet has antibacterial, antifungal and anthelmintic properties (Docampo and Moreno, 1990). In biology, it is used as a histological stain, particularly grams method for classifying bacteria (Hall *et al.*, 1966). It is also used as an alternative to fluorescent stains, which made it popular as a means of avoiding UV-induced DNA destruction when performing DNA cloning in vitro. In forensics, gentian violet was used to develop fingerprints. It is also used as a tissue stain in the preparation of light microscopy sections (Henneman and Kohn, 1975).

In laboratory, solutions containing crystal violet and formalin are often used to simultaneously fix and stain cells grown in tissue culture to preserve them and make them

easily visible, since most cells are colourless. It is also sometimes used as a cheap way to put identification markings on laboratory mice since many strains of lab mice are albino so the purple colour stays on their fur for several weeks (Henneman and Kohn, 1975). Industrially, it is used to dye paper and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers. It is also used to colourize diverse products such as fertilizers, anti-freezes, detergents, and leather jackets.

Therefore, potential human exposure to crystal violet could result from the consumption of treated fish and from working in the dye and aquaculture industries and also in the laboratories (Anderman and Clifton, 1993). Coloured dyes are not only carcinogenic, but also disturb life processes of living organisms in water. It is needed to remove these dyes before throwing them into receiving water bodies. Possible treatments such as chemical oxidation, electrochemical degradation and adsorption are used for this purpose (Whebi *et al.*, 2010, Alamddine and Jamal, 2009, Rammel *et al.*, 2011). In view of the above outlined important uses of this dye, hence there is need for further research in this area. Kinetics and mechanisms of the dye with oxyanions ( $\text{ClO}_3^-$ ,  $\text{HSO}_5^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) have been studied (Mohammed *et al.*, 2011; Kranti, 2011; Mohammed and Komolafe, 2010). The present work deals with the kinetics and mechanisms of the dye with oxyanions ( $\text{BrO}_3^-$ ,  $\text{IO}_4^-$ ,  $\text{ClO}^-$  and  $\text{S}_2\text{O}_5^{2-}$ ) in aqueous acidic medium.

The kinetics data generated and the subsequent mechanisms proposed will assist in the better understanding and more efficient utilization of the reactions of crystal violet and also complement the much needed kinetic information which may throw more light on the staining properties, dye fastness and the electron transfer properties of this dye with the aim of explaining and subsequently improving their physico-chemical properties.

## 1.8 Aim

The aim of this research work is to study the kinetics and mechanism of the redox reaction of crystal violet with oxidant  $\text{BrO}_3^-$ ,  $\text{IO}_4^-$ ,  $\text{ClO}^-$  and  $\text{S}_2\text{O}_5^{2-}$  as oxyanions in acid medium.

## 1.9 Objectives

The above aim would be achieved through the following objectives:

- a. determining the stoichiometry of the redox reaction,
- b. estimating the rate constant as well as obtain the order of the reaction,
- c. monitoring the effect of changes in acid concentration, ionic strength and added ions on the reaction rates,
- d. testing for intermediate complex formation and free radicals and
- e. deducing a plausible mechanism and assigning operative mechanism for the reaction.

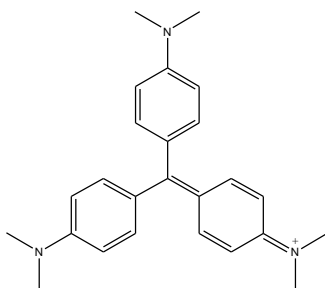


## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Reactions of Crystal Violet

Crystal violet (Gentian violet) with a molecular formula of  $C_{25}H_{30}N_3Cl$  is a triphenyl methane dye that is antimicrobial (Hall *et al.*, 1966). It is used as a bacteriostatic agent in medical solutions (Bale, 1981), and to treat skin infections by *Staphylococcus aureus* (Saji *et al.*, 1995).



**Structure of Crystal violet**

Crystal violet is a cationic dye. Cationic or basic dyes are dyes in which the chromophore is on the cation (Parameswaran *et al.* 1974). It is used as a dye and also possesses antibacterial, antifungal and anthelmintic properties which make it useful in dentistry (Gorgas *et al.* 1901). The dye differs from other triphenylmethanes in that the amino groups are methylated or substituted. Crystal violet is readily soluble in water and highly stable, with the absorption maximum of  $\lambda_{max} \approx 590$  nm. It is very important in biological stains for the study of bacteria and related microorganisms. The dye is also used as a constituent of culture media, as indicator and for laboratory diagnosis of disease (Docampo and Moreno, 1990).

The kinetic studies of the reaction of crystal violet ( $\text{CV}^+$ ) and chlorate ( $\text{ClO}_3^-$ ) was carried out in aqueous acidic medium, at a temperature of  $32 \pm 1^\circ\text{C}$ ;  $I = 0.50 \text{ mol dm}^{-3}$  ( $\text{NaCl}$ ),  $[\text{H}^+] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$  ( $\text{HCl}$ ) (Mohammed *et al.*, 2011). In the stoichiometry, one mole of the dye was consumed by two moles of  $\text{ClO}_3^-$ . The reaction was found to be first order in both the dye and the oxidant. The rate of redox reaction showed dependence on acid concentrations.

Rate law for the reaction has been proposed as:

$$\frac{-d[\text{CV}^+]}{dt} = (b[\text{H}^+])[\text{CV}^+][\text{ClO}_3^-] \quad (2.1)$$

The second order rate constant for the crystal violet  $-\text{ClO}_3^-$  reaction was found to be  $3.88 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The rate of reaction displayed zero salt effect and was not affected by changes in dielectric constant of the reaction medium. Added anions and cations catalysed the reaction. Results of the Michaelis-Menten analysis gave no evidence of intermediate complex formation. Based on the results obtained experimentally, the outersphere mechanism was proposed for the reaction.

The kinetics and mechanism of the reaction of crystal violet by peroxomonosulphate (oxone) has been reported by Kranti (2011). The reaction was studied under pseudo first order condition at constant temperature of  $25 \pm 0.1^\circ\text{C}$ . The stoichiometry was found to be one mole of crystal violet to two moles of oxone. The reaction was not affected by changes in the dielectric constant of the reaction medium and there was no evidence for the formation of free radicals in the mechanism of the reaction.

## 2.2 Reactions of metabisulphite ion

Metabisulphite ion or pyrosulphite ion is a good reducing agent whose compounds are used as preservative and antioxidant in food (EUFIC, 2007). Concentrated sodium metabisulphite can be used to remove tree stumps and it is a primary ingredient in campden tablets, used for wine and beer making to inhibit the growth of wild yeasts, bacteria and fungi (Miline, 2005). Some brands contain 98% sodium metabisulphite, and cause degradation of lignin in the stumps, facilitating its removal (OSHA, 2008).

In the study of the kinetics of reduction of rosaniline with sodium metabisulphite, one mole of rosaniline was consumed by one mole of the metabisulphite ion (Onu and Iyun, 2001). Second order rate constant was determined and the effect of acid on the rate of reaction showed two pathways, one which is acid dependent and the other which is acid independent.

$$K_{\text{obs}} = k_1 + k_2 [\text{H}^+]^{-1} \quad (2.2)$$

The rate of reaction displayed negative salt effect and there was no evidence of intermediate complex formation. Anions were found to catalyze the reaction, hence outersphere mechanism was proposed for the reaction.

The study of the kinetics of the reduction of potassium hexacyanoferrate(III) with sodium metabisulphite as a function of pH (varied between 2.6 to 4.7 using citric acid buffer system) and at temperatures. 15 °C, 20 °C, 25 °C and 30 °C, ionic strength maintained at 1.0 mol dm<sup>-3</sup> (KCl), a second order observed rate constant was found to follow two path; acid dependent and an inverse acid dependent paths (Abbas and Nabeel, 2010).

The kinetic data were explained by invoking radical mechanism in which the HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> formed HSO<sub>3</sub>· and SO<sub>3</sub>· Radicals. They proposed that an alternative redox process could

take place by a mechanism in which a fast reversible equilibrium is established between the hydrogen ions and hexacyanoferrate(III), followed by a slow reaction of the protonated species with the sulfite ion leading to the formation of sulfite free radical.

The kinetics and mechanism of the reduction of methylene blue with metabisulphite ion in acidic medium showed the stoichiometry of 1:3. The kinetic studies indicated first order dependence in both methylene blue and metabisulphite ion (Babatunde *et al.*, 2013). The rate of reaction was enhanced by increase in hydrogen ion concentration which conforms to equation (2.3) below.

$$K_2 = a + b [H^+] \quad (2.3)$$

Results from spectroscopic investigations and Michaelis-Menten plot showed no evidence of the formation of an intermediate complex. The mechanism of the reaction was therefore discussed in terms of outersphere mechanism.

The kinetic study of oxygen exchange between the sulfite ion and water (Betts and Voss, 1970) in which  $^{18}\text{O}$  was used as a stable trace 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 were obtained to be

$$k_2 = 7.00 \pm 0.21 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

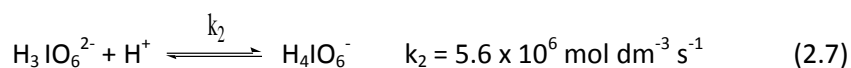
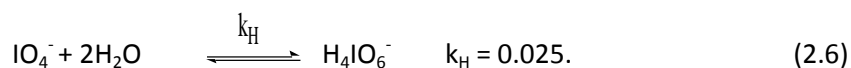
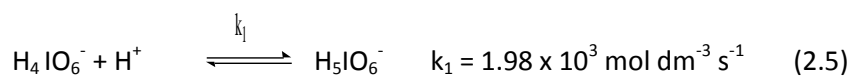
$$k_1 = 10^4 \text{ s}^{-1} \text{ at } 24.7^\circ\text{C} \text{ at an ionic strength of } 0.9 \text{ mol dm}^{-3}.$$



### 2.3 Reactions of periodate ion

Periodate has been used extensively in oxidations of organic as well as inorganic compounds (Sulfab, 1976; Sulfab and Abu Shaby, 1977). It has been found that periodate ion readily oxidizes both labile and inert complexes, possessing at least one bridging ligand. The majority of oxidation reaction of periodate has been found to proceed via the innersphere mechanism (Indelli *et al.*, 1966; Buchacek and Gordon, 1972; Buist, 1972; Kassim and Sulfab, 1981; Sulfab and Abdel-Khalek, 1981). This mechanism has been supported from <sup>13</sup>I labeled photometric studies for identification of intermediate in the oxidation of Co(II) complexes of EDTA, HEDTA and EDDA (Kassem and Sulfab 1978; Abdel Khalek and Sulfab, 1981).

The periodate ion in aqueous medium has been shown to exist in different species (Benson, 1969; Vivekananda and Ramachandra, 1982). These species include  $\text{H}_5\text{IO}_6^-$ ,  $\text{H}_4\text{IO}_6^{2-}$ ,  $\text{H}_3\text{IO}_6^{2-}$  and  $\text{IO}_4^-$  which are involved in the following equilibrium;



where  $k_1$ ,  $k_H$  and  $k_2$  are values at  $I = 0$  and  $k_3$  is a value at  $I = 1.0 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . However  $\text{H}_4\text{IO}_6^-$  and  $\text{IO}_4^-$  are the dominant and reactive species in acidic medium ( $\text{pH} = 4.2$ ) at  $I = 1.0 \text{ mol dm}^{-3}$  (Kustin and Lieberman, 1964).

The interest in periodate as an oxidant has been extended to organic compounds, particularly in the oxidation of phenols (Radhakrishnamurti *et al.*, 1976). For example, the

oxidation of 1, 2-diols by  $IO_4^-$  proceeds by way of a covalent link involving a cyclic intermediate, which corresponds to an innersphere mechanism (Buist, 1972).

The oxidation of 12-tungstocobaltate(II) with periodate ion in aqueous solution has been reported by El-Idris (1998). The reaction which was catalysed by Cu(II) ions was found to be of the outersphere type with the following rate law.

$$\frac{-d [Co^{II}W]}{dt} = 2k_3 [Co^{II}W][IO_4^-] [Cu^{2+}] \quad (2.9)$$

$$k_3 = a + b [H^+]$$

where  $k_3 = 3.5 \times 10^{-3} \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$ ,  $[H^+] = 0.02 - 0.2 \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  ( $NaClO_4$ ) and  $T = 24.5 + 0.1 \text{ }^\circ\text{C}$ .

The oxidation of Fe(II) by periodate ion in aqueous acidic solution proceeded via one electron transfer (El-Eziri and Sulfab, 1977). However, periodate is a two electron oxidant (I(VII) – I(V)) and therefore a concurrent two electron transfer is not ruled out. The two electrons could be abstracted from one Fe(II) with the formation of unstable Fe(IV) or from two Fe(II) (Sutin *et al.*, 1965). The dependence of rate on oxygen exchange and redox reactions on  $[H^+]$  like with oxyanions has been observed (Birk and Kozub, 1973). Thus in terms of the dependence of  $k_2$  on  $[H^+]$ , the commonly observed rate law is given as:

$$\frac{-d [IO_4^-]}{dt} = (k_2 + k_H [H^+]) [Fe(CN)_6^{4-}] [IO_4^-] \quad (2.10)$$

Onu *et al.*, (2009) studied the kinetics of the reduction of tetraoxoiodate(VII) by n-(2-hydroxyethyl)ethylenediamminetriacetatocobalt(II) ion in aqueous perchloric acid. The stoichiometry was found to be 2:1, the reaction was found to be first order with respect to both

oxidant and reductant concentrations and second order overall. The rate equation for the reaction was written as:

$$\frac{-d[\text{CoEDTAOH}_2]}{dt} = k_2[\text{CoHDTAOH}_2][\text{IO}_4^-] \quad (2.11)$$

where  $k_2 = 15.31 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

The kinetics and mechanism of oxidation of chromium(III) – tetraoxoarea complex by periodate ion was reported by Abdel-Khalek *et al.*, (1994). It was proposed that electron transfer proceeds through an innersphere mechanism via coordination of the  $\text{IO}_4^-$  to chromium(III). The reduction of I(VII) to I(V) seems to proceed by one electron transfer step. Such process has been reported for the Fe(II) and I(VII) reactions, where the formation of free radicals was ascertained (Symons, 1955).

The electron transfer reaction between diaquotetrakis(2,2' – bipyridine)  $\mu$ -oxodiruthenium(III) and  $\text{IO}_4^-$  have shown lack of evidence for innersphere mechanism (Lohdip, 1989). The rate law for the reaction was given by the expression.

$$\frac{-d}{dt}[\text{RuORu}^{4+}] = k_3 + Kk_2[\text{H}^+][\text{RuORu}^{4+}][\text{L}^-] \quad (2.12)$$

where  $\text{L}^-$  represents total periodate ( $\text{H}_4\text{IO}_6$  and  $\text{IO}_4^-$ ), with  $k_3 = 7.75 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}$ .

Therefore, outersphere mechanism was postulated for the reaction.

In the investigation of the kinetics and mechanism of indigo carmine by periodate ion (Edokpayi *et al.*, 2010), reported that two moles of indigo carmine were consumed by one mole of  $\text{IO}_4^-$ . Kinetic studies showed that the reaction is first order in oxidant and reductant

respectively and second order overall. The acid dependence studies showed that both protonated and deprotonated forms of the oxidant are reacting at the rate determining step. It was observed that, changes in ionic strength had no effect on the oxidation of indigo carmine by periodate ion.

The kinetics of the oxidation of Naphthol green B ( $\text{NGB}^{3-}$ ) by periodate ion has been studied by Myek *et al.*, (2013). The stoichiometry of  $\text{NGB}^{3-} : \text{IO}_4^-$  reaction was found to be 2:1. The reaction is first order with respect to both oxidant and the reductant concentrations. Polymerization test suggest the absence of free radicals in the reaction medium. Both added cations and anions inhibited the reaction rate. Outersphere mechanism was proposed for the reaction.

## 2.4 Reactions of Bromate Ion

Bromate is a strong oxidizing agent. Its redox reaction with both organic and inorganic substances has been studied (Birk, 1978; Jonnalagadda *et al.*, 1995; Lohdip *et al.*, 1996, Onu *et al.*, 2010). The rate of redox reactions of bromate have been shown to depend strongly on acid concentration (Birk and Kozub, 1978; Ayoko *et al.*, 1991). The hydrogen ion concentration dependence suggests that the oxidation reactions occur via two parallel pathways involving protonated and unprotonated species both reacting to give the product (Birk and Kozub, 1973, Lohdip *et al.*, 1995).

The commonly encountered acid dependence in the reactions of bromate in acidic medium has been attributed to the formation of species such as  $\text{HBrO}_3$  for first order dependence and  $\text{H}_2\text{BrO}_3^+$  for second order dependence, which then react at the rate determining step or decomposes to give  $\text{BrO}_2^+$  and  $\text{H}_2\text{O}$  as shown in the following equilibria.





Iyun and Asala, (1994) have studied the kinetics and mechanism of methylene blue oxidation by bromate ion and the stoichiometry of 1:5 was observed. The reaction was first order dependent with respect to both reactants. The rate law involves both acid dependent and acid independent pathways.

Also, the oxidation of thymol blue by bromate ion has been studied (Jonnalagadda *et al.*, 1995). The reaction exhibit a complex mechanism in that the stoichiometry of the reaction was 3:2 (thymol blue: bromate) at low bromate concentration and 4:5 when bromate was in excess.

The kinetics of the oxidation of pyrocatechol violet by bromate ions has been carried out in aqueous hydrochloric acid medium (Adetoro *et al.*, 2010). The reaction was first order with respect to oxidant and reductant concentrations. Changes in the concentration of hydrogen ions and the ionic strength of reaction medium were found to affect the reaction. Added anions and cations inhibited the reaction rate respectively. The results of spectroscopic and kinetic investigation showed no intermediate complex was formed in the course of the reaction.

Redox kinetics of the reaction of hydroxylamine hydrochloride ( $\text{H}_2\text{NOH.HCl}$ ) and  $\text{BrO}_3^-$  was carried out in aqueous acidic medium (Idris *et al.*, 2010). The reaction had a stoichiometry of 1:1.3, first order kinetics in both  $[\text{NH}_3\text{OH}^+]$  and  $[\text{BrO}_3^-]$ , dependent on acid concentrations,

showed positive salt effect, catalysis due to anions and absence of evidence of intermediate complex formation.

Rate equation for the reaction has been proposed as:

$$-d \frac{[NH_3OH^+]}{dt} = (a[H^+]) [NH_3OH^+] [BrO_3^-] \quad (2.16)$$

The second order rate constant for the reaction was found to be  $0.233 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

## 2.5 Reactions of hypochlorite ion

Hypochlorites are very strong oxidizing agents with low stability. They react with many organic and inorganic compounds. Reaction with organic compound is very exothermic. The hypochlorite ion is also known as chlorate (I) anion ( $\text{ClO}^-$ ).

The oxidation of bromide ion by hypochlorite ion was investigated by Farkas *et al.*, (1949). The reaction was carried out at pH range 10.8-13.2 and the progress of the reaction was monitored by titrimetric methods.



The rate-determining step identified was the reaction between HOCl and  $\text{Br}^-$  with a rate constant of  $2.95 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $25^\circ \text{C}$ . Their proposed mechanism implies nucleophilic attack by  $\text{Br}^-$  at oxygen, which is equivalent to an  $\text{OH}^-$  transfer between  $\text{Cl}^-$  and  $\text{Br}^-$ .



The oxidation of tryptophan to 3-indoleacetaldehyde with sodium hypochlorite was investigated with  $^{14}\text{C}$  19abeled DL-tryptophan (Thomas *et al.*, 1981). The reaction was performed under pseudo first order conditions. From the pH dependence of the reaction, it was concluded that only the unprotonated tryptophan is converted to aldehyde. Varying the pH between 8.5 and 11.0 and the temperature in the range of 298K to 318K did not alter the selectivity of the reaction as confirmed by TLC of the product (purity  $\geq 90\%$ ).

Jiann-Kuo, (1987) investigated the reduction of potassium hypochlorite using a rotating cylindrical platinum cathode. First-order kinetics with respect to the activity of  $\text{H}^+$  and  $\text{ClO}^-$  was observed. The mechanism of reduction of  $\text{ClO}^-$  involved formation of  $\text{HClO}$  followed by the transfer of an electron to the acid as shown below:



The kinetics and mechanism of the reaction of azide with hypochlorite was studied by Eric *et al.*, (2010). The reaction stoichiometry was found to be 1:2 ( $\text{HOCl} : \text{N}_3$ ) and was found to

proceeds by a key intermediate chlorine azide,  $\text{ClN}_3$  which subsequently decomposes by reaction with the second azide molecule in the rate determining step:



$$(k = 0.52 \pm 0.04 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, 25 \text{ }^\circ\text{C } \mu = 0.1 \text{ mol dm}^{-3}).$$

They concluded that hypochlorite is not recommended for treatment of concentrated azide waste due to the formation of the toxic chlorine azide intermediate under acidic conditions and the slow kinetics under basic conditions.

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Materials

All solutions were prepared with distilled water except otherwise stated. Analytical grade reagents were used throughout this work without further purification. Hydrochloric acid was used to investigate the effect of hydrogen ion on the reaction for the crystal violet-metabisulphite, crystal violet-bromate and crystal violet-periodate systems, while perchloric acid was used for crystal violet-hypochlorite system. Sodium chloride was used to maintain a constant ionic strength for each run in the crystal violet- metabisulphite, crystal violet-bromate and crystal violet-periodate systems, while sodium perchlorate was used for crystal violet-

hypochlorite system. Sodium metabisulphite, potassium bromate, sodium periodate and sodium hypochlorite were the redox reagents used.

### **3.1.1 Crystal violet**

The dye, crystal violet, analar grade, was obtained from Aldrich chemical company. Stock solution of the dye was prepared by weighing 0.0408g of the dye and dissolving in a 100cm<sup>3</sup> of volumetric flask with distilled water and making up to the mark to obtain 1.0 x 10<sup>-3</sup> solution. The electronic spectrum of the solution was run using a Jenway 6405 uv/vis spectrophotometer within a wavelength range of 400-700 nm. From the spectrum, the wavelength of maximum absorption ( $\lambda_{\max}$ ) of 585 nm was obtained. This is close to the value of 590 nm reported in the literature (Adams and Rosenstein, 1914).

### **3.1.2 Preparation of 1.0 mol dm<sup>-3</sup> sodium metabisulphite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) solution**

Standard solution (1.0 mol dm<sup>-3</sup>) of sodium metabisulphite was prepared by dissolving 4.7525g of the salt in 25 cm<sup>3</sup> volumetric flask and made up to the mark with distilled water.

### **3.1.3 Preparation of 0.1 mol dm<sup>-3</sup> potassium bromate (KBrO<sub>3</sub>) solution**

Weighed quantity of potassium bromate (1.670g) was dried in an oven for one hour at 110 °C and dissolved in a 100 cm<sup>3</sup> volumetric flask. The solution was made up with distilled water.

### **3.1.4 Preparation of 1.0 mol dm<sup>-3</sup> sodium periodate (NaIO<sub>4</sub>) solution**

Stock solution of  $1.0 \text{ mol dm}^{-3}$  was prepared by dissolving 10.70g of  $\text{NaIO}_4$  in a  $100 \text{ cm}^3$  volumetric flask wrapped with aluminum foil to prevent photochemical decomposition (Symons, 1955; Vivekananda and Ramachhandran, 1982).

### **3.1.5 Preparation of Sodium hypochlorite ( $\text{NaClO}$ ) solution**

Standard stock solution of sodium hypochlorite was prepared by transferring  $3.00 \text{ cm}^3$  of 10 %  $\text{NaClO}$  (density  $1.2065 \text{ g cm}^{-3}$ ) into a  $50 \text{ cm}^3$  volumetric flask and making up to the mark with distilled water to obtain  $0.1 \text{ mol dm}^{-3}$  solutions.

### **3.1.6 Preparation of standard solution of hydrochloric acid**

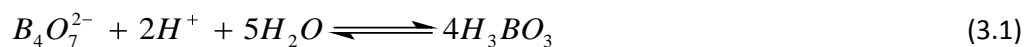
Stock solution of hydrochloric acid was made by diluting 37% of hydrochloric acid of specific gravity 1.18 in volumetric flask. The solution was standardized volumetrically using sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and methyl orange as indicator.

### **3.1.7 Preparation of $0.1 \text{ mol dm}^{-3} \text{Na}_2 \text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$**

An accurate quantity (3.82g) Borax was weighed and dissolved in  $100 \text{ cm}^3$  distilled water in a standard volumetric flask to give a  $0.1 \text{ mol dm}^{-3}$  solution. This was used as primary standard for  $\text{HClO}_4$ .

### **3.1.8 Preparation of standard solution of perchloric Acid ( $\text{HClO}_4$ )**

Stock solution of perchloric acid was made by the diluting 70% of perchloric acid (density 1.67g/cm<sup>3</sup>) in a volumetric flask. The HClO<sub>4</sub> was standardized by volumetric analysis using sodium tetraborate decahydrate (Borax) as primary standard. Methyl red was used as indicator, from the results, the molarity of the acid was determined according to the equation of the reaction below (Vogel, 1978).



### 3.1.9 Preparation of standard sodium perchlorate (NaClO<sub>4</sub>) solution

Sodium perchlorate was prepared by dissolving 28.092g in 100 cm<sup>3</sup> volumetric flask with distilled water and making up to the mark to obtain 2.0mol dm<sup>-3</sup> solution.

### 3.1.10 Preparation of standard sodium chloride solution

Sodium chloride was prepared by dissolving 11.70 g of the salt with distilled water in 100 cm<sup>3</sup> volumetric flask to obtain 2.0 mol dm<sup>-3</sup> solutions.

### 3.1.11 Preparation of sodium carbonate solution

Stock solution of 0.10 mol dm<sup>-3</sup> sodium carbonate was obtained by dissolving 1.06g of Na<sub>2</sub>CO<sub>3</sub> with distilled water. This solution was used as a primary standard in the standardization of hydrochloric acid.

### 3.1.12 Preparation of salt solutions

Stock solutions of sodium ethanoate, magnesium chloride, sodium methanoate and calcium chloride were prepared by dissolving a known amount of each salt in a known volume of distilled water.

## 3.2 Methods

### 3.2.1 Stoichiometric studies

The stoichiometry of the reactions was determined by spectrophotometric titration, using the mole ratio method. The concentration of crystal violet ( $\text{CV}^+$ ) was kept constant at  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$  (for bromate ion system),  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$  (for periodate ion system),  $[\text{H}^+] = 5.0 \times 10^{-3}$  and  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  (for metabisulphite and hypochlorite systems) respectively,  $l = 0.50 \text{ mol dm}^{-3}$  for all the systems,  $\lambda_{\text{max}} = 585 \text{ nm}$ ,  $T = 28 \pm 1 \text{ }^\circ\text{C}$  for  $\text{BrO}_3^-$ ,  $\text{IO}_4^-$  and  $\text{ClO}^-$  and  $30 \pm 1 \text{ }^\circ\text{C}$  for  $\text{S}_2\text{O}_5^{2-}$ .  $[\text{BrO}_3^-]$ ,  $[\text{IO}_4^-]$ ,  $[\text{ClO}^-]$  and  $[\text{S}_2\text{O}_5^{2-}]$  was varied in the range  $(0.25 - 4) \times 10^{-5} \text{ mol dm}^{-3}$ .

The reacting mixtures were allowed to go to completion as indicated by steady value of absorbance observed over a period of two days. The final absorbances were taken and the graphs of absorbance against mole ratio were plotted, the stoichiometry was then evaluated from the graphs.

### 3.2.2 Kinetic measurements

The rates of the reaction were monitored following the rate of decrease in absorbance of the dye at  $\lambda_{\text{max}} = 585 \text{ nm}$  on a Jenway uv/vis spectrophotometer. All kinetic measurements were performed under pseudo first order conditions with the concentration of crystal violet



kept constant at  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  and that of the other reductants/oxidants maintained at least 20 fold in excess over that of the dye. The following experimental conditions were maintained for the respective systems studied.

- Crystal violet – metabisulphite system:

$[\text{S}_2\text{O}_5^{2-}] = (2-16) \times 10^{-3} \text{ mol dm}^{-3}$  ( $\text{Na}_2\text{S}_2\text{O}_5$ ),  $[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  (HCl),  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) and  $T = 30 \pm 1^\circ\text{C}$ .

- Crystal violet – bromate system

$[\text{BrO}_3^-] = (1-9) \times 10^{-3} \text{ mol dm}^{-3}$  ( $\text{KBrO}_3$ ),  $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$  (HCl),  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) and  $T = 28 \pm 1^\circ\text{C}$ .

- Crystal violet- periodate system:

$[\text{IO}_4^-] = (2-16) \times 10^{-3} \text{ mol dm}^{-3}$  ( $\text{NaIO}_4$ ),  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$  (HCl),  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) and  $T = 28 \pm 1^\circ\text{C}$

- Crystal violet – hypochlorite system:

$[\text{ClO}^-] = (2-14) \times 10^{-4} \text{ mol dm}^{-3}$  ( $\text{NaClO}$ ),  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$  ( $\text{HClO}_4$ ),  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) and  $T = 28 \pm 1^\circ\text{C}$

The pseudo first order constants for the reactions were obtained from the plots of the  $\log (A_t - A_\infty)$  versus time,  $t$  (where  $A_\infty$  and  $A_t$  are the absorbance at the end of the reaction and at time,  $t$ ) and 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 the relation:

$$k_2 = k_1 / [\text{Oxyanions}]$$

3.1

### 3.2.3 Effect of $[H^+]$ on the reaction rate

The effect of  $[H^+]$  on the rate of the reactions was investigated keeping the concentration of the reactants constant while varying the  $[H^+]$ . The following experimental conditions were maintained for the four systems:

- Crystal violet-metabisulphate system:

$$[S_2O_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}, [H^+] = (1-8) \times 10^{-3} \text{ mol dm}^{-3}, I = 0.5 \text{ mol dm}^{-3} T = 30 \pm 1^\circ\text{C}$$

- Crystal violet – bromate system:

$$[BrO_3^-] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, [H^+] = (0.6-2.4) \times 10^{-2} \text{ mol dm}^{-3}, I = 0.5 \text{ mol dm}^{-3} T = 28 \pm 1^\circ\text{C}$$

- Crystal violet – periodate system:

$$[IO_4^-] = 6.0 \times 10^{-2} \text{ mol dm}^{-3} [H^+] = (2-14) \times 10^{-2}, \text{ mol dm}^{-3}, I = 0.5 \text{ mol dm}^{-3} T = 28 \pm 1^\circ\text{C}$$

- Crystal violet – hypochlorite system:

$$[ClO^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}, [H^+] = (4-16) \times 10^{-4} \text{ mol dm}^{-3}, I = 0.5 \text{ mol dm}^{-2} T = 28 \pm 1^\circ\text{C}$$

The order of reaction with respect to hydrogen ion concentration was obtained as the slope of the plot of  $\log k_1$ , against  $\log [H^+]$ . Variation of acid dependent rate constant with  $[H^+]$  was obtained by plotting  $k_2$  against  $[H^+]$ .

### 3.2.4 Effect of ionic strength and dielectric constant of reaction medium on the reaction rate

The effect of ionic strength on the rate of the reaction was investigated over a range of  $(0.2 - 1.0) \text{ mol dm}^{-3}$  using NaCl for  $\text{BrO}_3^-$ ,  $\text{IO}_4^-$  and  $\text{S}_2\text{O}_5^{2-}$  and  $\text{NaClO}_4$  for  $\text{ClO}^-$ , while other reaction conditions were kept constant. Effect of changes in dielectric constant of the reaction medium on the reaction rate was investigated by adding  $0.10 - 0.80 \text{ cm}^3$  (accounting for 2 - 16%) acetone to the reaction mixture, while all other conditions were kept constant. A plot of  $\log k_2$  against  $1/D$  gives the relationship between the second order rate constant and the dielectric constant  $D$ .

### 3.2.5 Effect of added ions on the reaction rate

The effect of added ions on the reaction rate was studied by addition of  $(10 - 100) \times 10^{-3} \text{ mol dm}^{-3}$  of the ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ) while keeping all other parameters constant.

### 3.2.6 Test for intermediate complex

The spectra of the reaction mixtures were obtained over a wavelength range of 500 - 700 nm. This was carried out in order to determine whether there is significant shift in  $\lambda_{\text{max}}$  or enhancement of peak resulted as the reaction progressed. Michaelis-Menten plot of  $1/k_1$  versus  $1/[\text{oxidant}]$  or  $1/[\text{reductant}]$  were also made.

### 3.2.7 Test for free radicals

To a partially oxidized reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion for each system, about  $5 \text{ cm}^3$  of acrylamide was added followed by

large excess of methanol to initiate free radical polymerization. A control experiment was carried out by adding acrylamide to each of the reactants separately. Formation of gelatinous precipitate indicates presence of free radicals.

### **3.2.8 Product analyses**

Presence of  $\text{SO}_4^{2-}$  (reduction product of  $\text{S}_2\text{O}_5^{2-}$ ),  $\text{Br}_2$  or  $\text{Br}^-$  (reduction product of bromate),  $\text{IO}_3^-$  (reduction product of  $\text{IO}_4^-$ ),  $\text{Cl}^-$  (reduction product of  $\text{ClO}^-$ ) were tested by qualitative inorganic analysis (Vogel 1961, Jeffery, 1991).

## **CHAPTER FOUR**

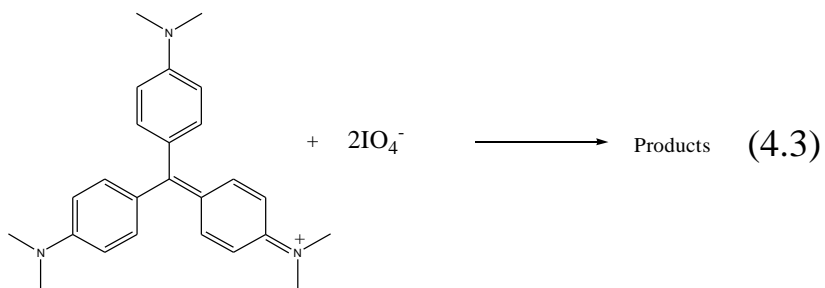
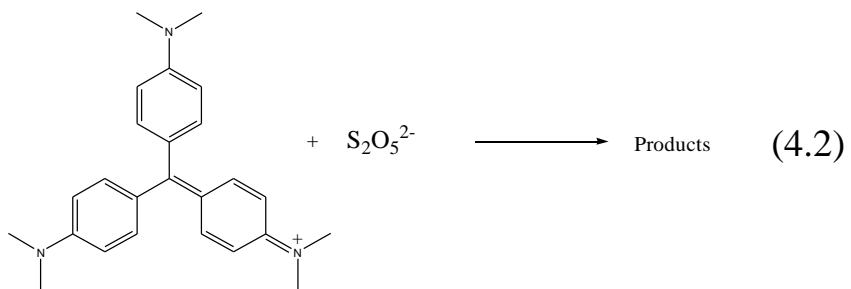
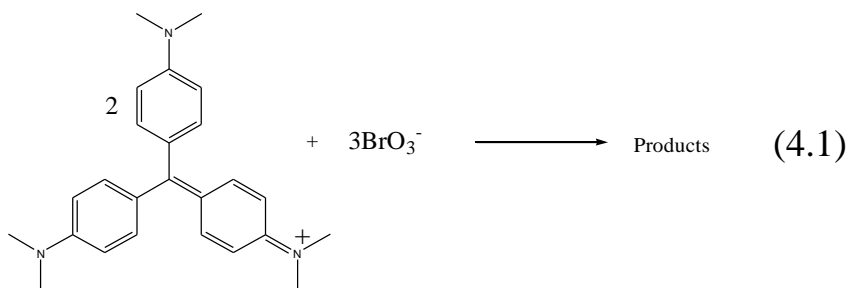
### **4.0 RESULTS**

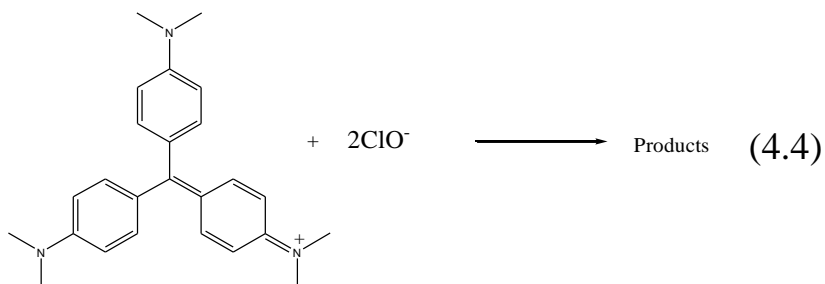
#### **4.1 Stoichiometry**

The results of the stoichiometric investigations indicate that one mole of crystal violet is consumed by one mole of metabisulphite ion, two moles of crystal violet consumed three moles of bromate ion, while one mole of crystal violet consumed two moles each of periodate ion and

hypochlorite ion respectively. The titration curves from which the stoichiometries of each of the systems were determined are presented in Figures (4.1-4.4).

Based on the above results, the overall equations for the redox reactions can be represented in equations (4.1-4.4).

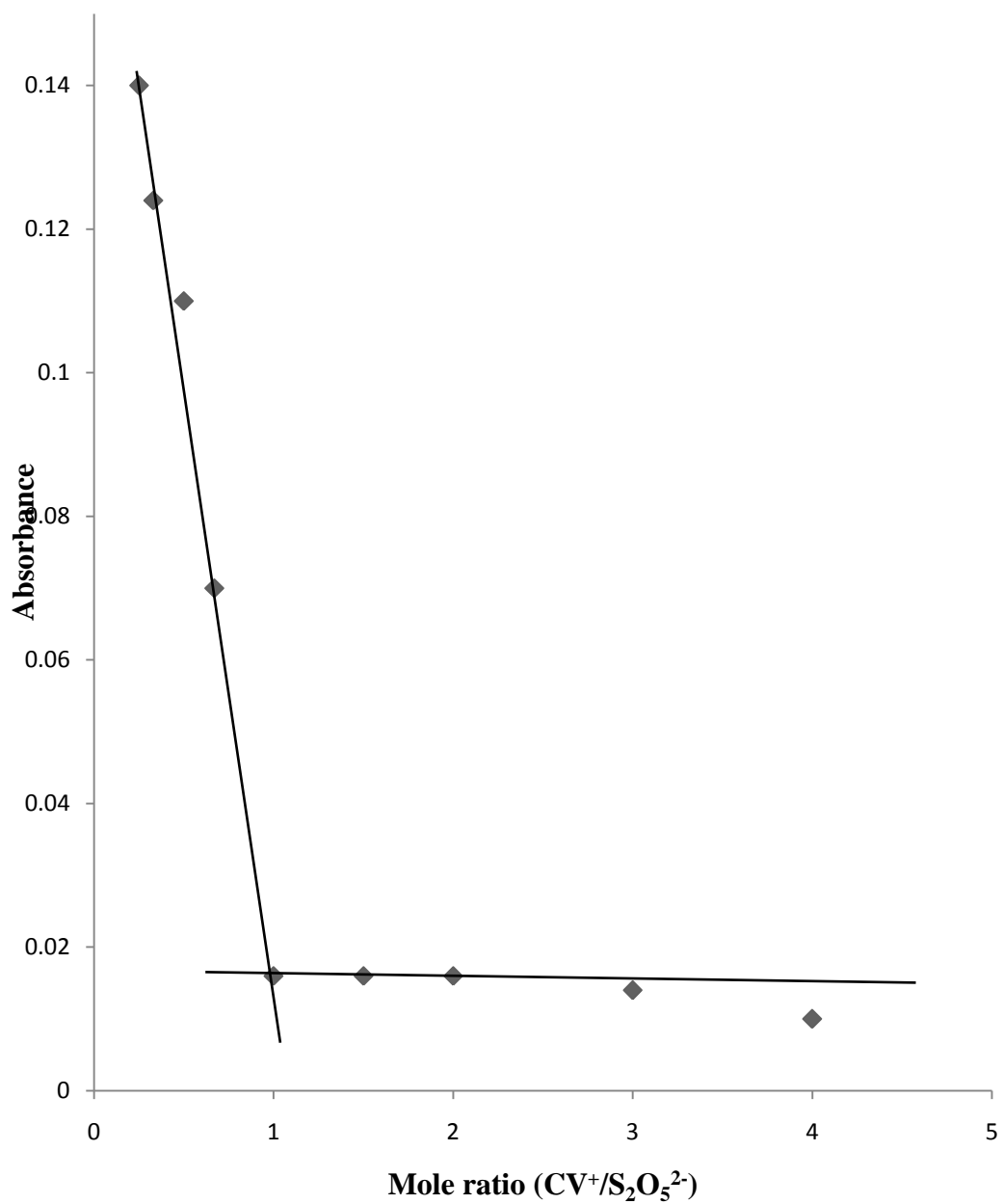




#### 4.2 Determination of Order of the Reactions with Respect to the Reactants

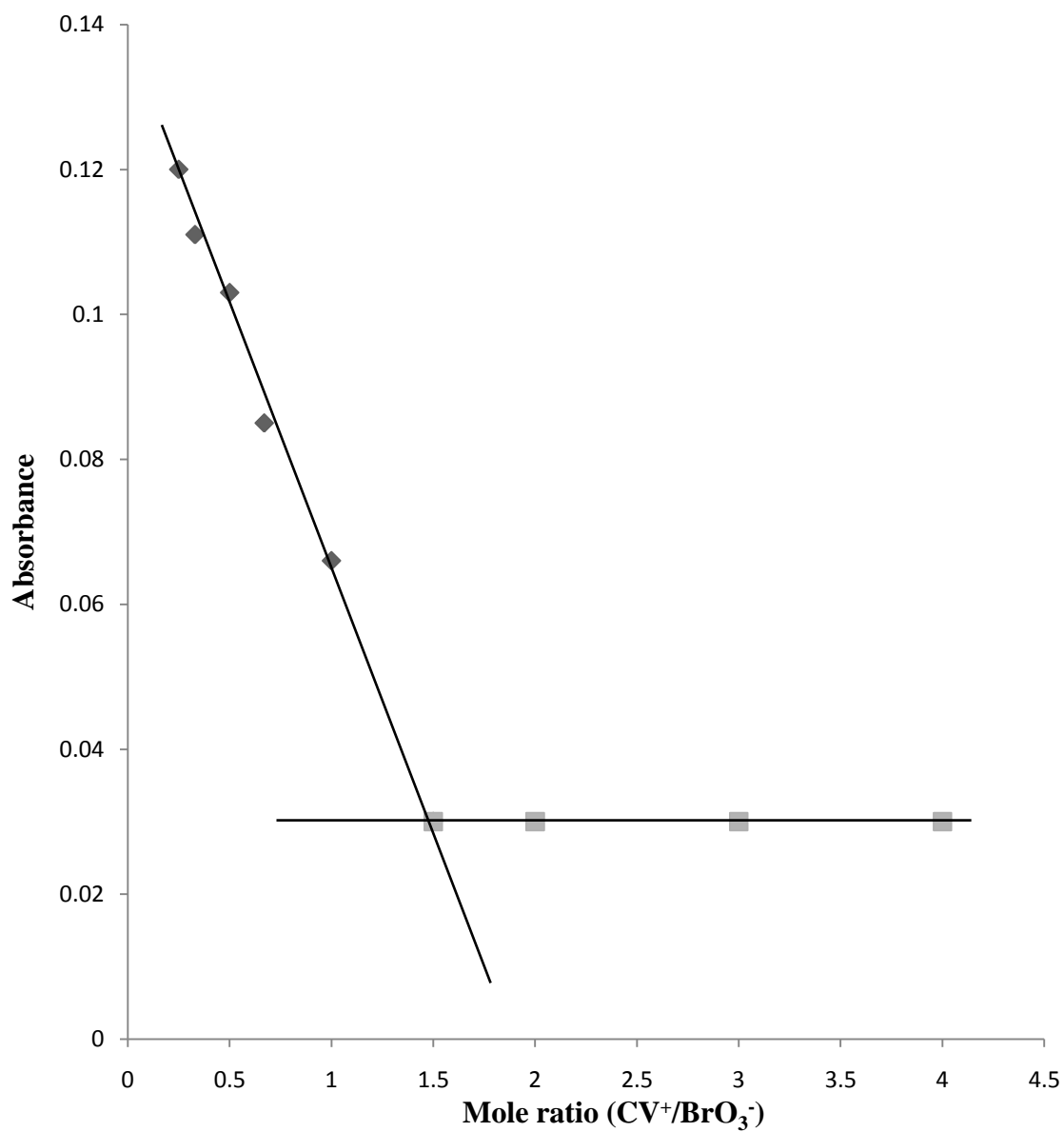
The pseudo-first order plot of  $\log (A_t - A_\infty)$  versus time were linear to about 90% extent of the reaction ( $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and at the end of the reaction respectively). The linearity of these plots indicates that these reactions are first order with respect to  $[CV^+]$ . The typical plots are shown in Figures (4.5-4.8). The pseudo-first order rate constant,  $k_1$  were calculated from the slopes of these plots and are reported on Tables (4.1-4.4).

Plots of  $k_1$  versus concentration of oxyanions of  $S_2O_5^{2-}$ ,  $BrO_3^-$ , and  $ClO^-$  at constant  $[H^+]$  were linear, Figures (4.9-4.11), showing that the rate of the reaction is first

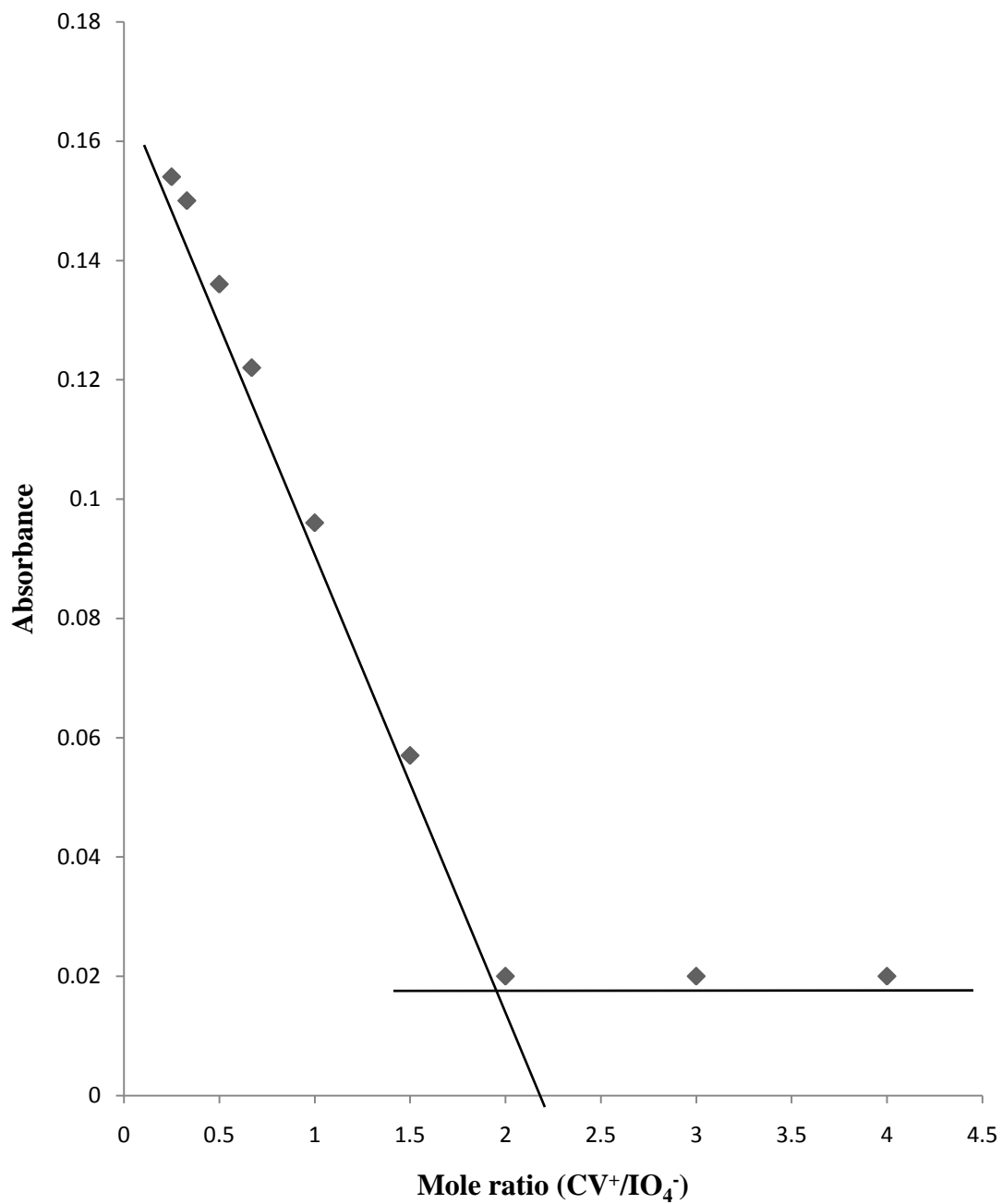


**Figure 4.1:** Plot of absorbance versus mole ratio for the redox reaction of crystal violet with metabisulphite ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 30 \pm 1 \text{ }^\circ\text{C}$

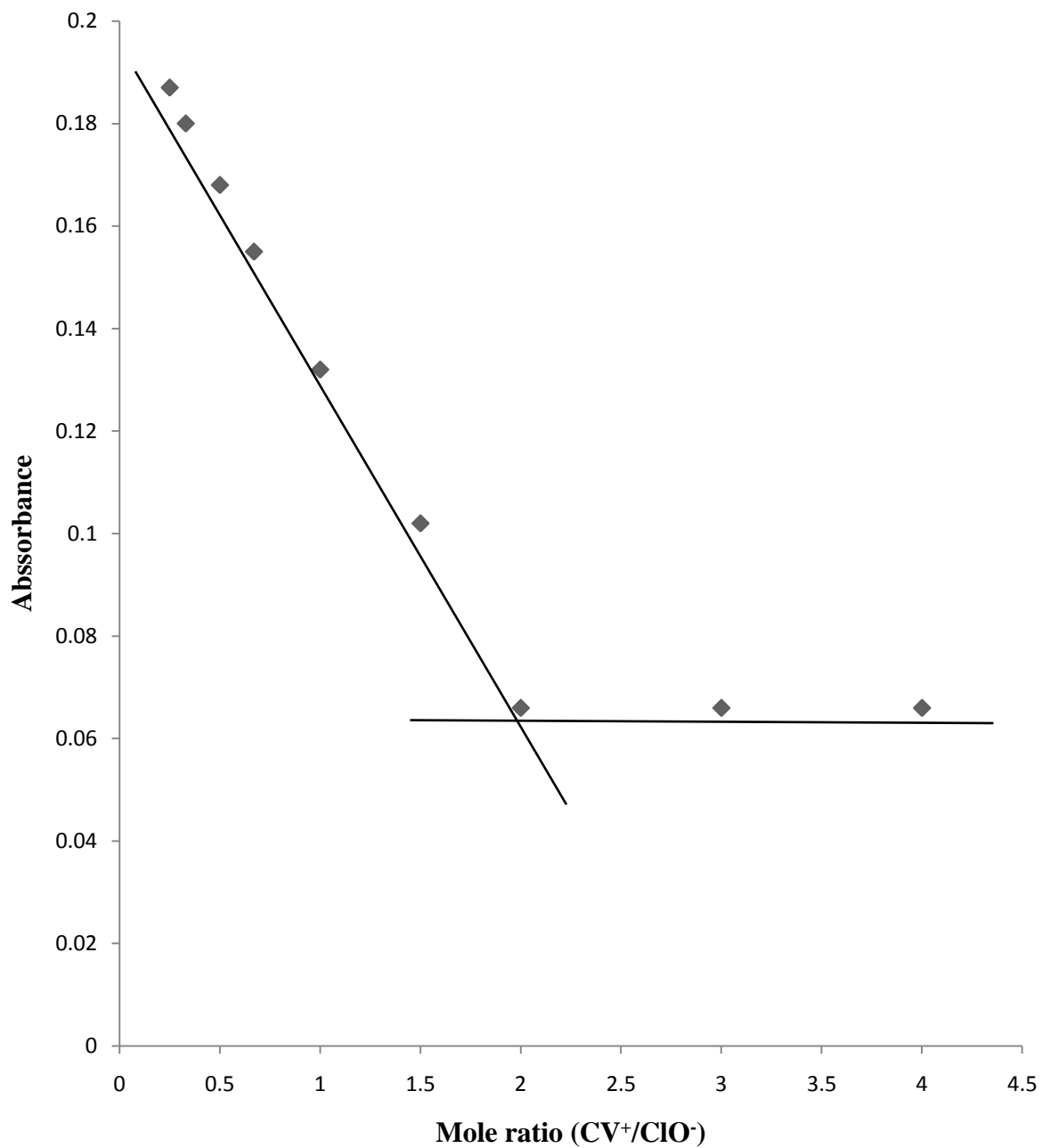




**Figure 4.2:** Plot of absorbance versus mole ratio for the redox reaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 31 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.3:** Plot of absorbance versus mole ratio for the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.4:** Plot of absorbance versus mole ratio for the redox reaction of crystal violet with hypochlorite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

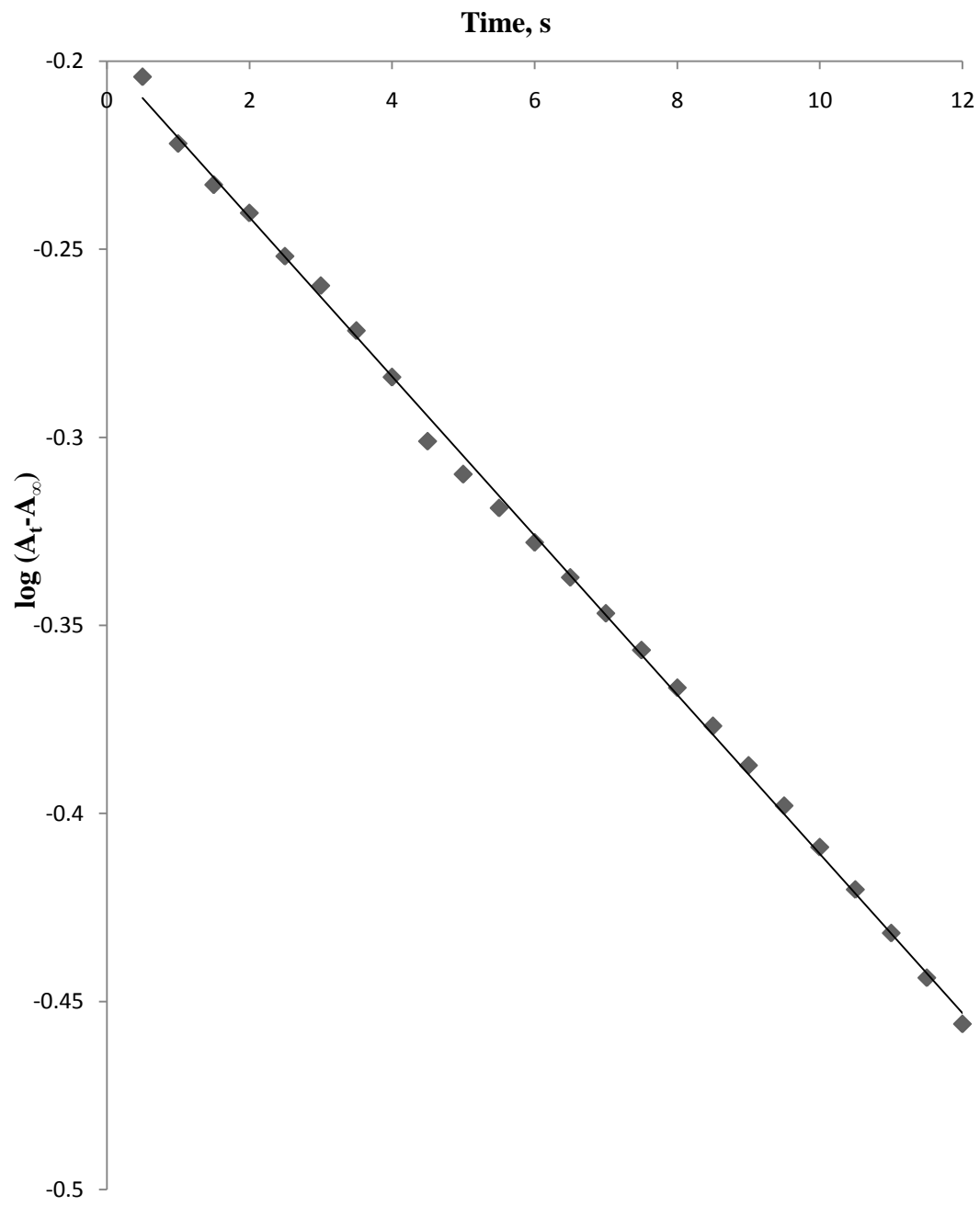


Figure 4.5: Typical pseudo-first order plot for the redox reaction of crystal violet with metabisulphite ions at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_5^{2-}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 30 \pm 1 \text{ }^\circ\text{C}$

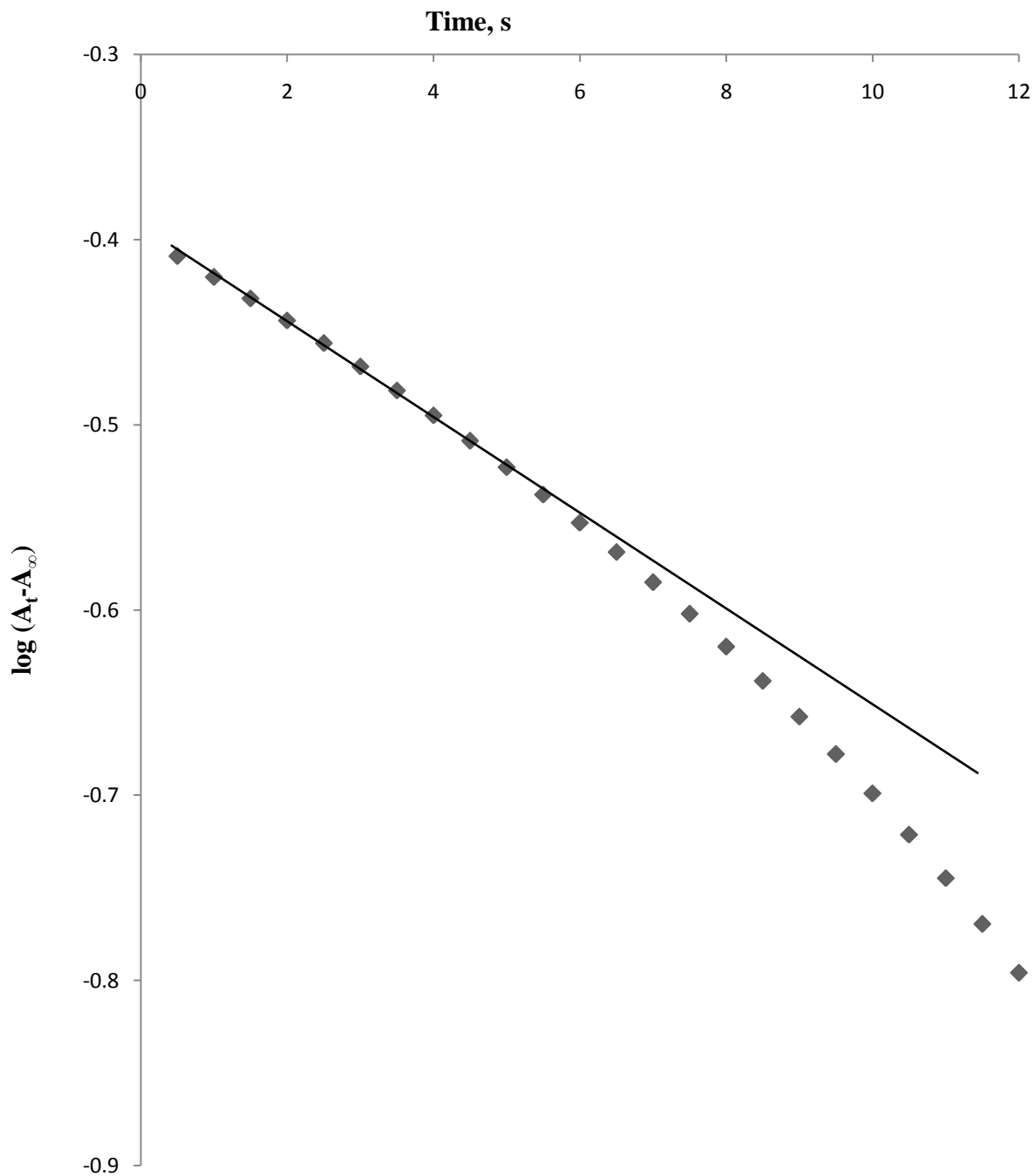
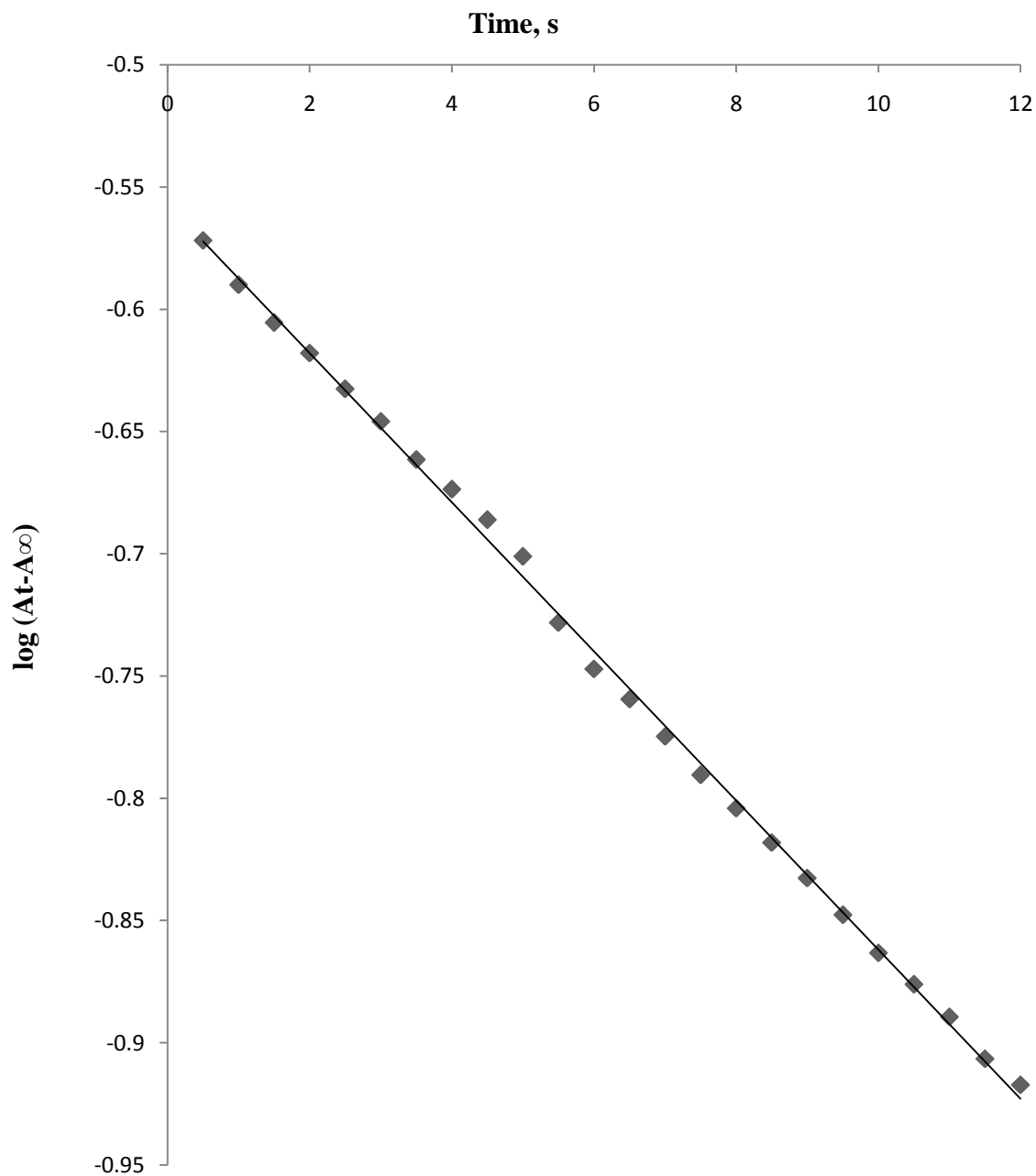


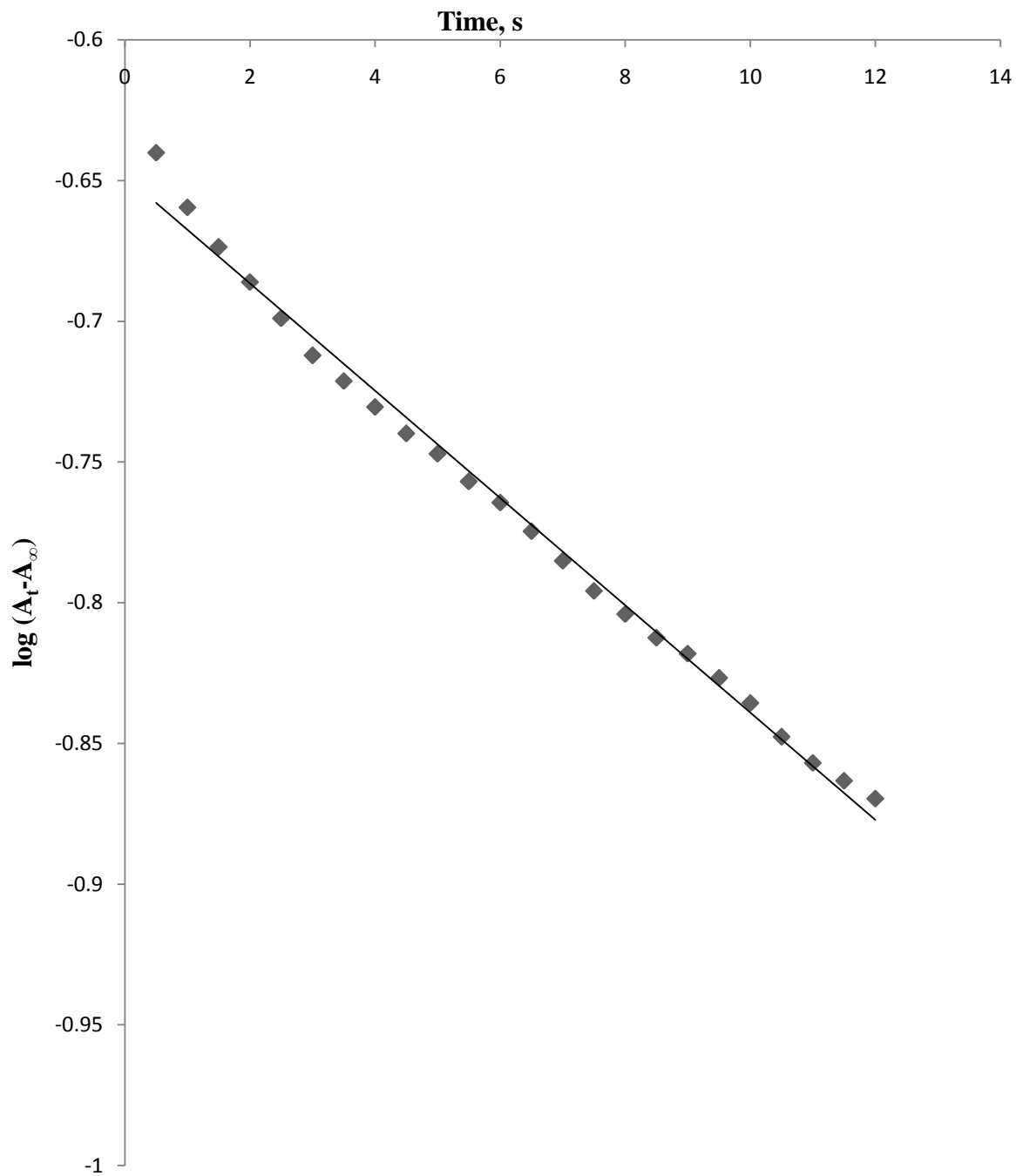
Figure 4.6: Typical pseudo-first order plot for the redox reaction of crystal violet with bromate ions at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[BrO_3^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm$

1 °C



**Figure 4.7:** Typical pseudo-first order plot for the redox reaction of crystal violet with periodate ions at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{IO}_4^-] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm$

**1 °C**



**Figure 4.8:** Typical pseudo-first order plot for the redox reaction of crystal violet with hypochlorite ions at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Table 4.1:** Pseudo-first order and second order rate constants for the redox reaction of crystal violet with metabisulphite ions in aqueous HCl medium at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $T = 30 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 585 \text{ nm}$

$10^3[S_2O_5^{2-}]$ , $\text{mol dm}^{-3}$	$10^3[H^+]$ , $\text{mol dm}^{-3}$	$l$ , $\text{mol dm}^{-3}$	$10^2k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
2.00	1.00	0.50	4.790	23.95
4.00	1.00	0.50	9.420	23.55
6.00	1.00	0.50	14.39	23.99
8.00	1.00	0.50	18.46	23.08
10.00	1.00	0.50	23.03	23.03
12.00	1.00	0.50	28.74	23.95
14.00	1.00	0.50	33.50	23.93
16.00	1.00	0.50	36.90	23.06
10.00	1.00	0.50	23.03	23.03
10.00	2.00	0.50	12.90	12.90
10.00	3.00	0.50	9.070	9.070
10.00	4.00	0.50	6.910	6.910
10.00	5.00	0.50	5.410	5.410
10.00	6.00	0.50	4.610	4.610
10.00	7.00	0.50	3.680	3.680
10.00	8.00	0.50	2.880	2.880
10.00	1.00	0.30	35.48	35.48

10.00	1.00	0.40	27.54	27.54
10.00	1.00	0.50	23.03	23.03
10.00	1.00	0.60	19.95	19.95
10.00	1.00	0.70	16.98	16.98
10.00	1.00	0.80	14.79	14.79
10.00	1.00	0.90	12.88	12.88
10.00	1.00	1.00	11.75	11.75

**Table 4.2:** Pseudo-first order and second order rate constants for the redox reaction of crystal violet with bromate ions in aqueous HCl medium at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $T = 28 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 585 \text{ nm}$

$10^3[\text{BrO}_3^-],$ $\text{mol dm}^{-3}$	$10^2[\text{H}^+], \text{mol dm}^{-3}$	$l, \text{mol dm}^{-3}$	$10^2k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
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1.00	2.00	0.50	3.850	38.50
2.00	2.00	0.50	7.670	38.35
3.00	2.00	0.50	11.56	38.53
4.00	2.00	0.50	15.36	38.40
5.00	2.00	0.50	19.42	38.84
6.00	2.00	0.50	23.30	38.84
7.00	2.00	0.50	26.61	38.01
8.00	2.00	0.50	30.70	38.38
9.00	2.00	0.50	34.55	38.39
8.00	0.60	0.50	3.410	4.263
8.00	0.80	0.50	3.880	4.850
8.00	1.00	0.50	7.670	9.588
8.00	1.20	0.50	11.22	14.025
8.00	1.40	0.50	15.49	19.363
8.00	1.60	0.50	22.39	27.988
8.00	1.80	0.50	28.18	35.225
8.00	2.00	0.50	30.70	38.375
8.00	2.20	0.50	33.24	41.550
8.00	2.40	0.50	53.73	67.163
8.00	2.00	0.30	21.53	26.913
8.00	2.00	0.40	25.30	31.625

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8.00	2.00	0.50	30.70	38.375
8.00	2.00	0.60	35.73	44.663
8.00	2.00	0.70	43.96	54.950
8.00	2.00	0.80	50.48	63.100
8.00	2.00	0.90	53.34	66.675

**Table 4.3:** Pseudo-first order and second order rate constants for the redox reaction of crystal violet with hypochlorite ions in aqueous HClO<sub>4</sub> medium at [CV<sup>+</sup>] = 1.0x10<sup>-5</sup> mol dm<sup>-3</sup>, T = 28 ± 1 °C and λ<sub>max</sub> = 585 nm

10 <sup>4</sup> [ClO <sup>-</sup> ], mol dm <sup>-3</sup>	10 <sup>3</sup> [H <sup>+</sup> ], mol dm <sup>-3</sup>	I, mol dm <sup>-3</sup>	10 <sup>1</sup> k <sub>1</sub> , s <sup>-1</sup>	k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
2.00	1.00	0.50	1.040	52.00

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4.00	1.00	0.50	2.070	51.75
6.00	1.00	0.50	3.060	51.00
8.00	1.00	0.50	4.080	51.00
10.00	1.00	0.50	5.180	51.80
12.00	1.00	0.50	6.220	51.83
14.00	1.00	0.50	7.190	51.36
8.00	0.40	0.50	1.980	24.75
8.00	0.60	0.50	2.530	31.63
8.00	0.80	0.50	3.610	45.13
8.00	1.00	0.50	4.080	51.00
8.00	1.20	0.50	5.770	72.13
8.00	1.40	0.50	7.020	87.75
8.00	1.60	0.50	8.750	109.38
8.00	1.00	0.30	4.060	50.75
8.00	1.00	0.40	4.050	50.63
8.00	1.00	0.50	4.080	51.00
8.00	1.00	0.60	4.070	50.88
8.00	1.00	0.70	4.080	51.00
8.00	1.00	0.80	4.060	50.75
8.00	1.00	0.90	4.100	51.25

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**Table 4.4:** Pseudo-first order rate constants for the redox reaction of crystal violet with periodate ions in aqueous HCl medium at  $[CV^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 28 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 585 \text{ nm}$

$10^3[\text{IO}_4^-], \text{ mol dm}^{-3}$	$10^2[\text{H}^+], \text{ mol dm}^{-3}$	$I, \text{ mol dm}^{-3}$	$10^2k_1, \text{ s}^{-1}$
2.00	5.00	5.00	6.89
4.00	5.00	5.00	6.90
6.00	5.00	5.00	6.89
8.00	5.00	5.00	6.81
10.00	5.00	5.00	6.92
12.00	5.00	5.00	6.89
14.00	5.00	5.00	6.89
16.00	5.00	5.00	6.89
6.00	2.00	5.00	3.20
6.00	4.00	5.00	6.61
6.00	5.00	5.00	6.89
6.00	6.00	5.00	8.96
6.00	8.00	5.00	12.16
6.00	10.00	5.00	15.24
6.00	12.00	5.00	19.07
6.00	14.00	5.00	20.27

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6.00	5.00	0.30	4.44
6.00	5.00	0.40	5.37
6.00	5.00	0.50	6.89
6.00	5.00	0.60	8.66
6.00	5.00	0.70	12.51
6.00	5.00	0.80	15.96

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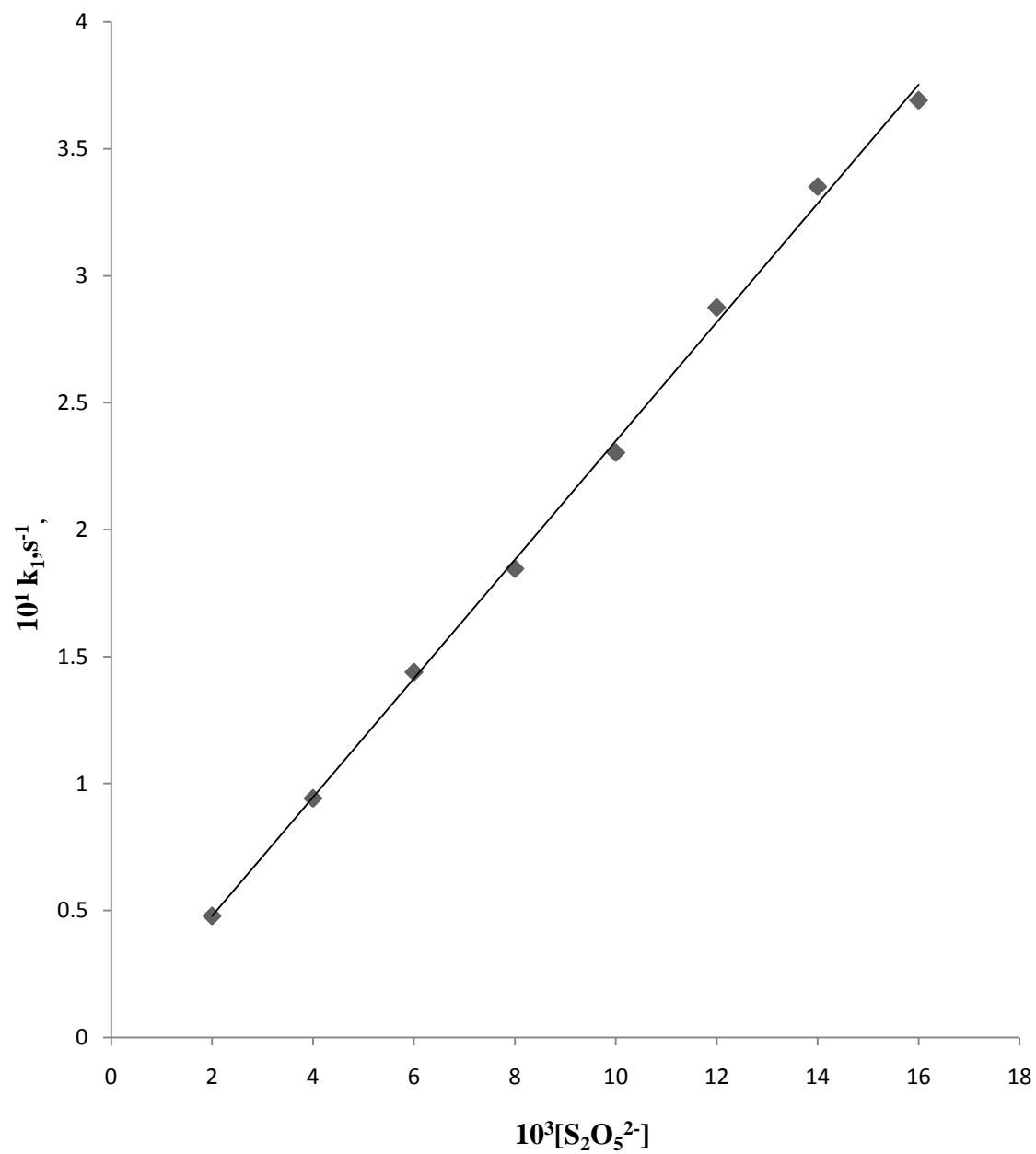


Figure 4.9: Plot of  $k_1$  versus  $[S_2O_5^{2-}]$  for the reaction of crystal violet and metabisulphite ion



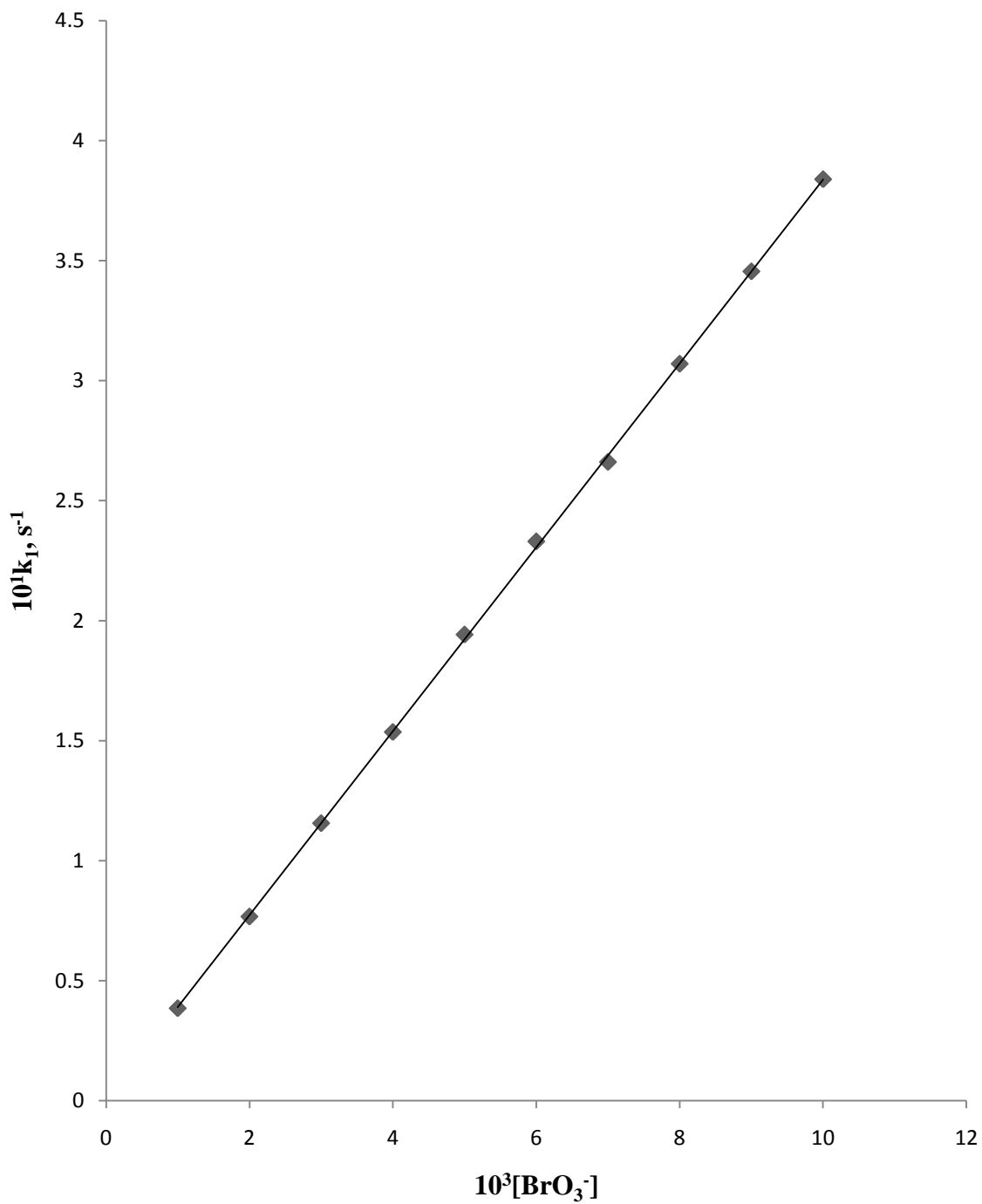


Figure 4.10: Plot of  $k_1$  versus  $[\text{BrO}_3^-]$  for the reaction of crystal violet and bromate ion

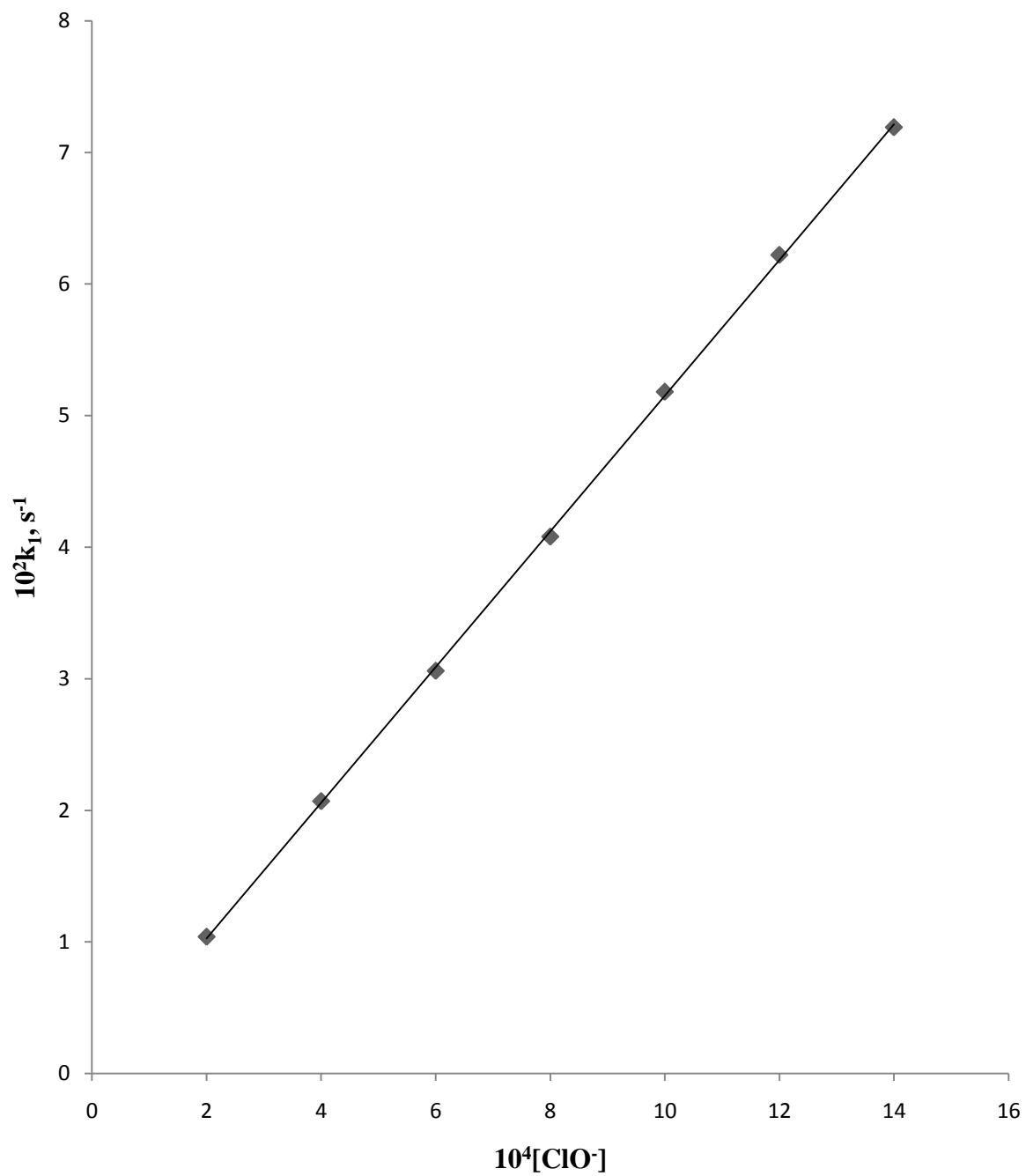


Figure 4.11: Plot of  $k_1$  versus  $[\text{ClO}^-]$  for the reaction of crystal violet and hypochlorite ion

order with respect to  $[S_2O_5^{2-}]$ ,  $[BrO_3^-]$  and  $[ClO^-]$ . Similarly, least square plots of  $\log k_1$  versus  $\log [S_2O_5^{2-}]$ ,  $[BrO_3^-]$  and  $[ClO^-]$  gave slopes of 0.99, 1.03 and 1.00 respectively.

This observation further proved that the order of the redox reaction with respect to  $[S_2O_5^{2-}]$ ,  $[BrO_3^-]$  and  $[ClO^-]$  are each unity. The plots are represented in Figures (4.12-4.14). The reaction is second order overall in these three systems, and the second order rate constants was determined from  $k_2 = k_1 / [\text{oxyanions}]$  (oxyanions =  $S_2O_5^{2-}$ ,  $BrO_3^-$ , or  $ClO^-$ ) and were found to be fairly constant, Tables (4.1-4.3).

For the periodate ion ( $IO_4^-$ ) system, the rate of the reaction was found not to vary with the concentration of the oxyanions ( $IO_4^-$ ). Thus the reaction was found to be zero order in  $[IO_4^-]$  within the range investigated, there was no enhancement of the rate even at high  $[IO_4^-] \geq 12 \times 10^{-2} \text{ mol dm}^{-3}$ . The  $k_1$  for the system was found not to vary; result is presented in Table 4.4.

On the basis of the above observations, the rate laws for these reactions can therefore be written as:

$$\frac{-d[CV^+]}{dt} = k_2[\text{oxyanions}][CV^+] \quad (4.5)$$

For metabisulphite, bromate and hypochlorite ion systems, and

$$\frac{-d[CV^+]}{dt} = k_1[CV^+] \quad (4.6)$$

for periodate ion system.

The second order rate constant for the various systems is;

For crystal violet- $\text{S}_2\text{O}_5^{2-}$  system:  $k_2 = (23.57 \pm 0.45) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

For crystal violet- $\text{BrO}_3^-$  system:  $k_2 = (38.47 \pm 0.26) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

For crystal violet- $\text{ClO}^-$  system:  $k_2 = (5.53 \pm 0.41) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

For crystal violet- $\text{IO}_4^-$  system:  $k_1 = (6.89 \pm 0.032) \times 10^{-2} \text{ s}^{-1}$

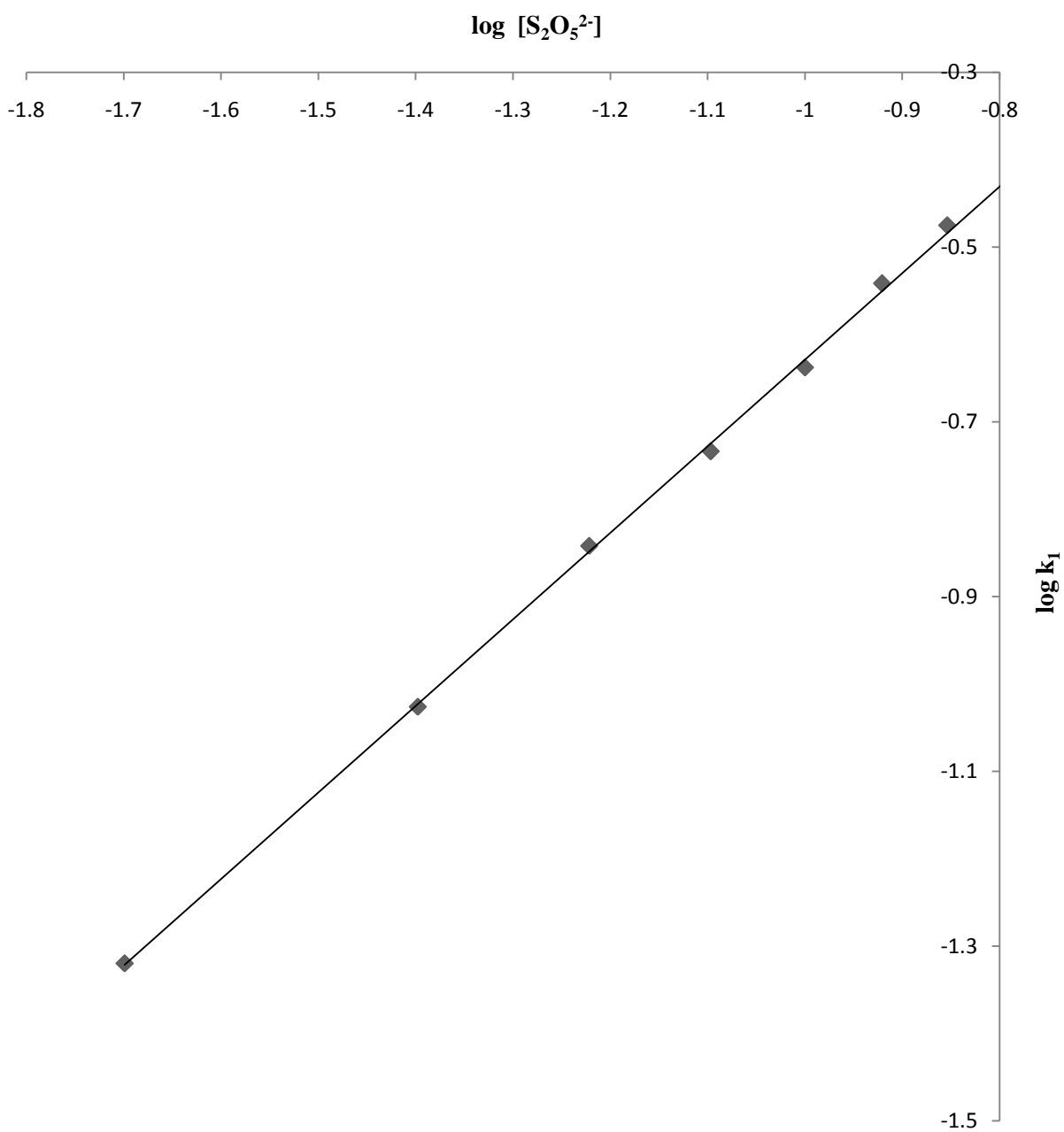


Figure 4.12: Pseudo-first order plot of  $\log k_1$  versus  $\log [S_2O_5^{2-}]$  for the redox reaction of crystal violet with metabisulphite ions at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 585 \text{ nm}$  and  $T = 30 \pm 1 \text{ }^\circ\text{C}$

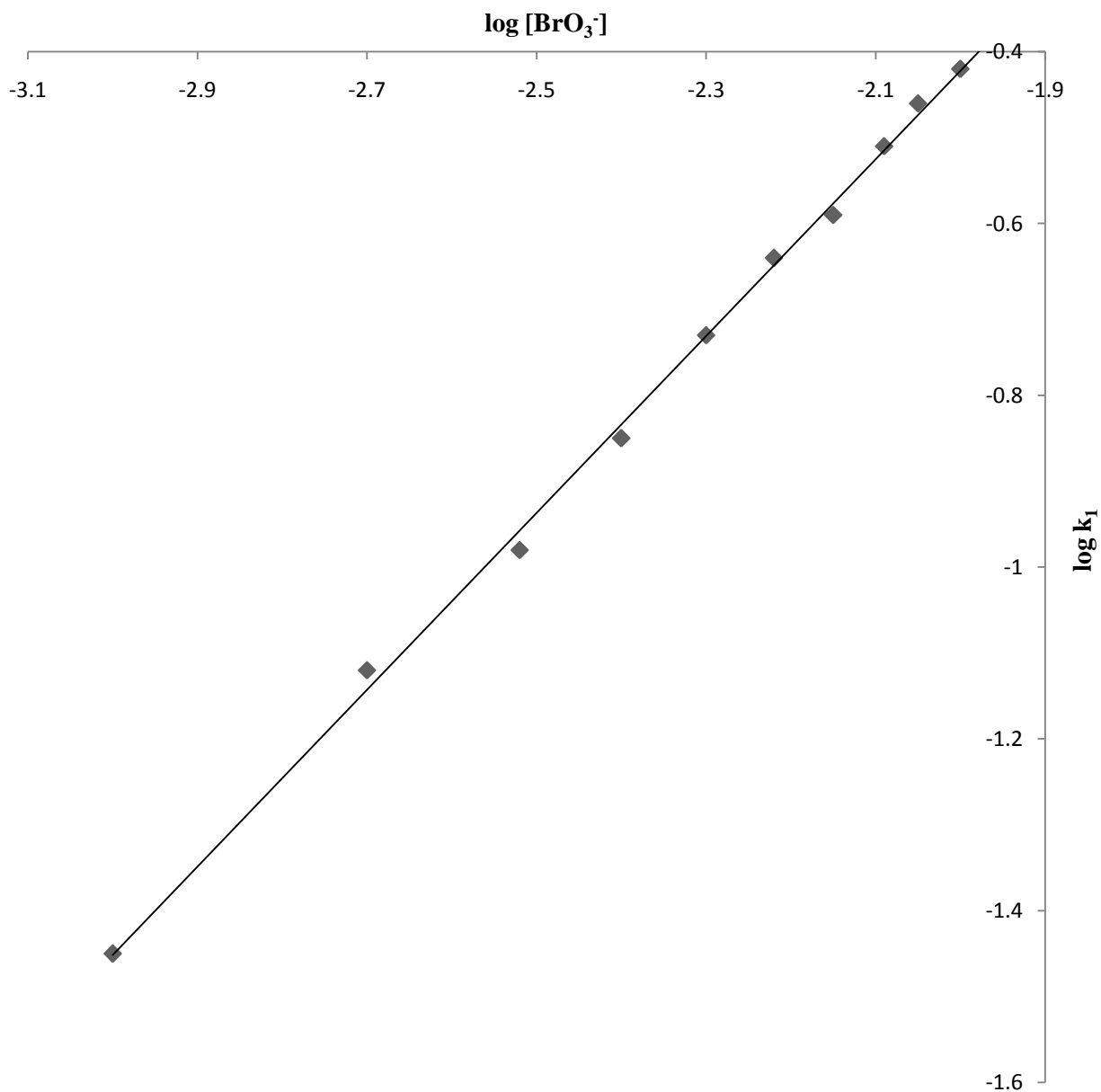
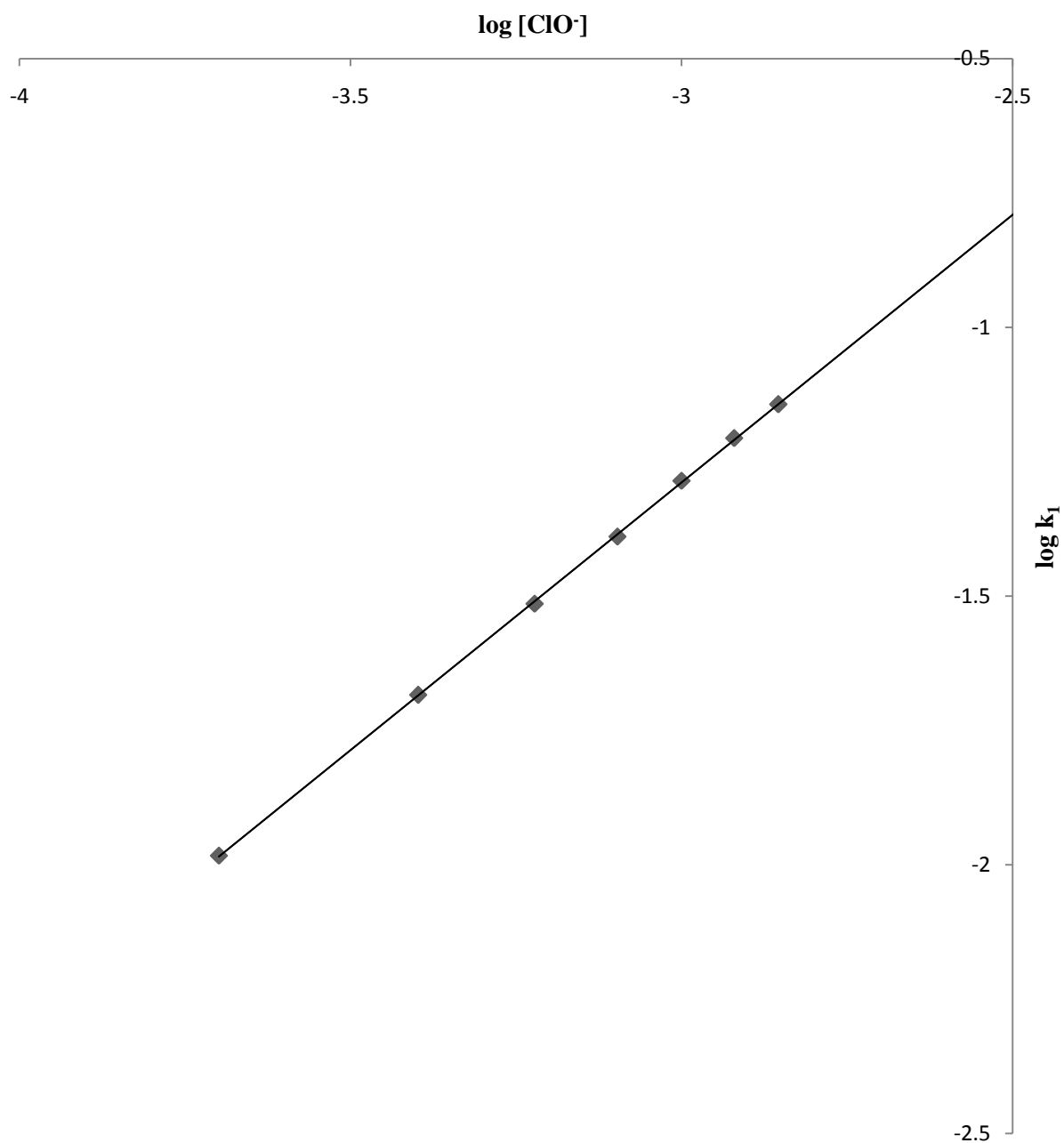


Figure 4.13: Pseudo-first order plot of  $\log k_1$  versus  $\log [BrO_3^-]$  for the redox reaction of crystal violet with bromate ions at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 585 \text{ nm}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.14:** Pseudo-first order plot of  $\log k_1$  versus  $\log [\text{ClO}^-]$  for the redox reaction of crystal violet with hypochlorite ions at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 585 \text{ nm}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

### 4.3 Effect of Hydrogen ion Concentration on the Rates of the Reactions

For the crystal violet-  $\text{BrO}_3^-$ , crystal violet-  $\text{ClO}^-$  and crystal violet- $\text{IO}_4^-$  systems, the rate of the reactions were found to increase with increase in hydrogen ion concentration in the range investigated, while for the crystal violet-  $\text{S}_2\text{O}_5^{2-}$  system, the rate of the reaction was found to be inversely influenced by hydrogen ion concentration. These are reported in Tables (4.1-4.4). Least square plots of  $\log k_1$  versus  $\log[\text{H}^+]$  were linear for all the systems with slopes of -0.97, 2.03, 0.97 and 1.08 for crystal violet-  $\text{S}_2\text{O}_5^{2-}$ , crystal violet-  $\text{BrO}_3^-$ , crystal violet-  $\text{IO}_4^-$  and crystal violet- $\text{ClO}^-$  systems respectively (Figures 4.15-4.18). This indicates that the order with respect to  $[\text{H}^+]$  in these reactions is first order for metabisulphite, periodate and hypochlorite ions systems and second order for bromate ion system.

Least square plot of  $k_2$  versus  $[1/\text{H}^+]$  for crystal violet- $\text{S}_2\text{O}_5^{2-}$  system had intercept, least square plot of  $k_2$  versus  $[\text{H}^+]^2$  for the crystal violet- $\text{BrO}_3^-$  and least square plot  $k_1$  versus  $[\text{H}^+]$  for crystal violet- $\text{IO}_4^-$  systems also had intercepts but plot of  $k_2$  versus  $[\text{H}^+]$  for crystal-violet- $\text{ClO}^-$  system passed through the origin (Figures 4.19-4.22)

The acid dependent rate constant can be represented by equation (4.7) for the  $\text{CV}^+$ - $\text{S}_2\text{O}_5^{2-}$  reaction, equation (4.8) for the  $\text{CV}^+$ - $\text{BrO}_3^-$  reaction, equation (4.9) for the  $\text{CV}^+$ -  $\text{IO}_4^-$  reaction and equation (4.10) for the  $\text{CV}^+$ -  $\text{ClO}^-$  reaction respectively.

$$K_2 = a + b[\text{H}^+]^{-1} \quad (4.7)$$

$$k_2 = c + d[\text{H}^+]^2 \quad (4.8)$$

$$k_1 = e + f[H^+] \quad (4.9)$$

$$k_2 = g[H^+] \quad (4.10)$$

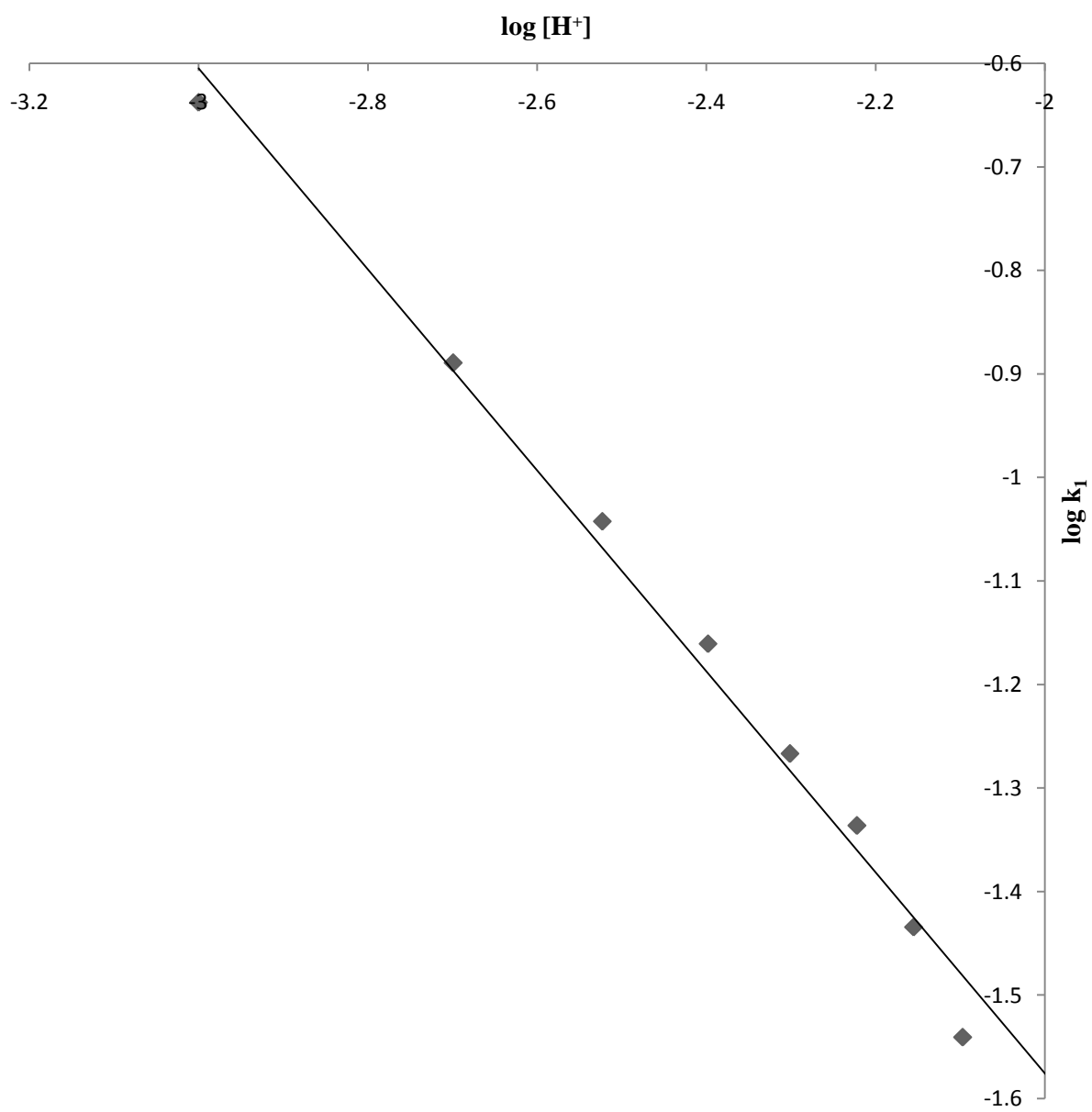




Figure 4.15: Plot of  $\log k_1$  versus  $\log [H^+]$  for the redox reaction of crystal violet with metabisulphite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 30 \pm 1 \text{ }^\circ\text{C}$

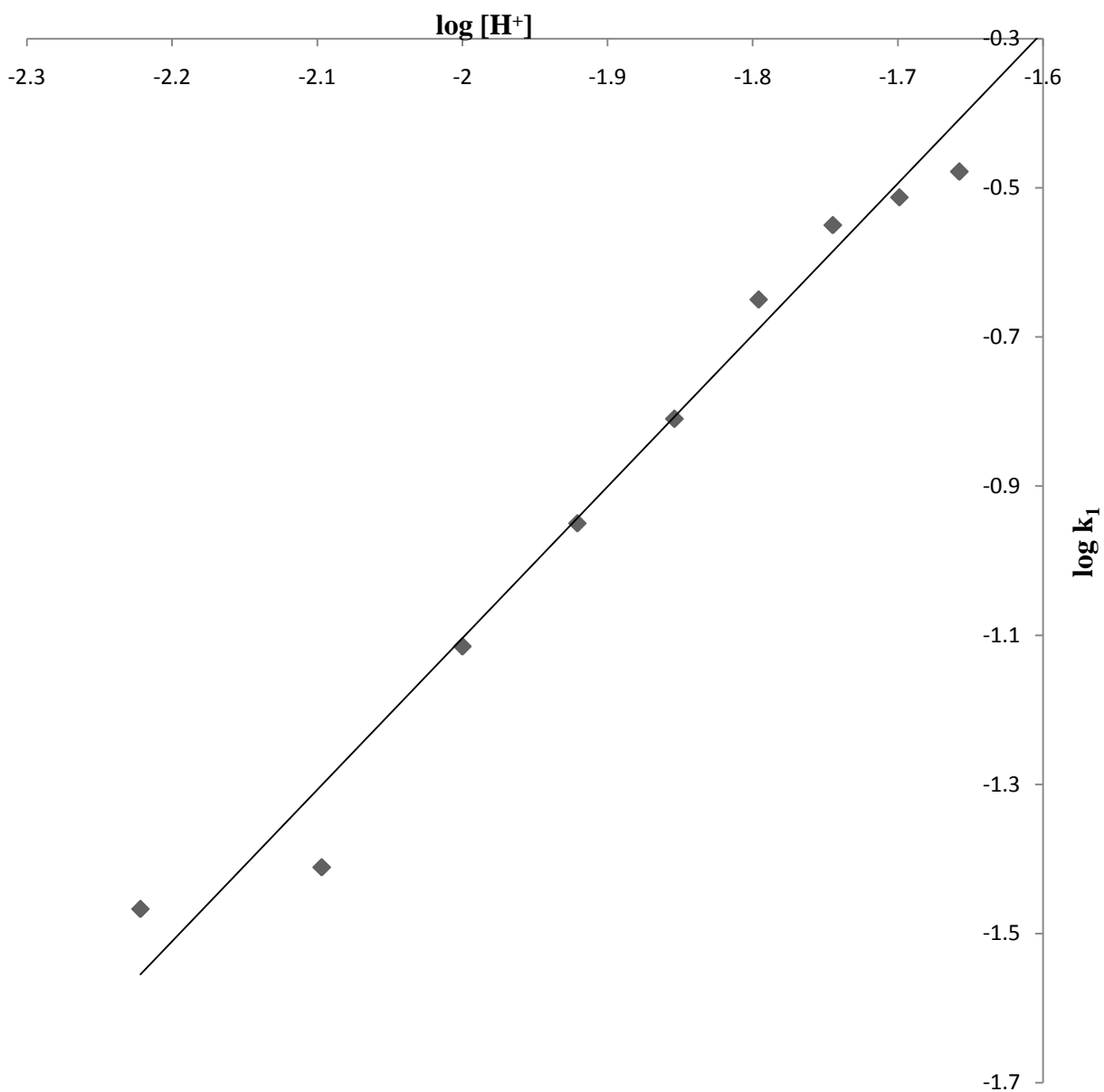


Figure 4.16: Plot of  $\log k_1$  versus  $\log [H^+]$  for the redox reaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[BrO_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

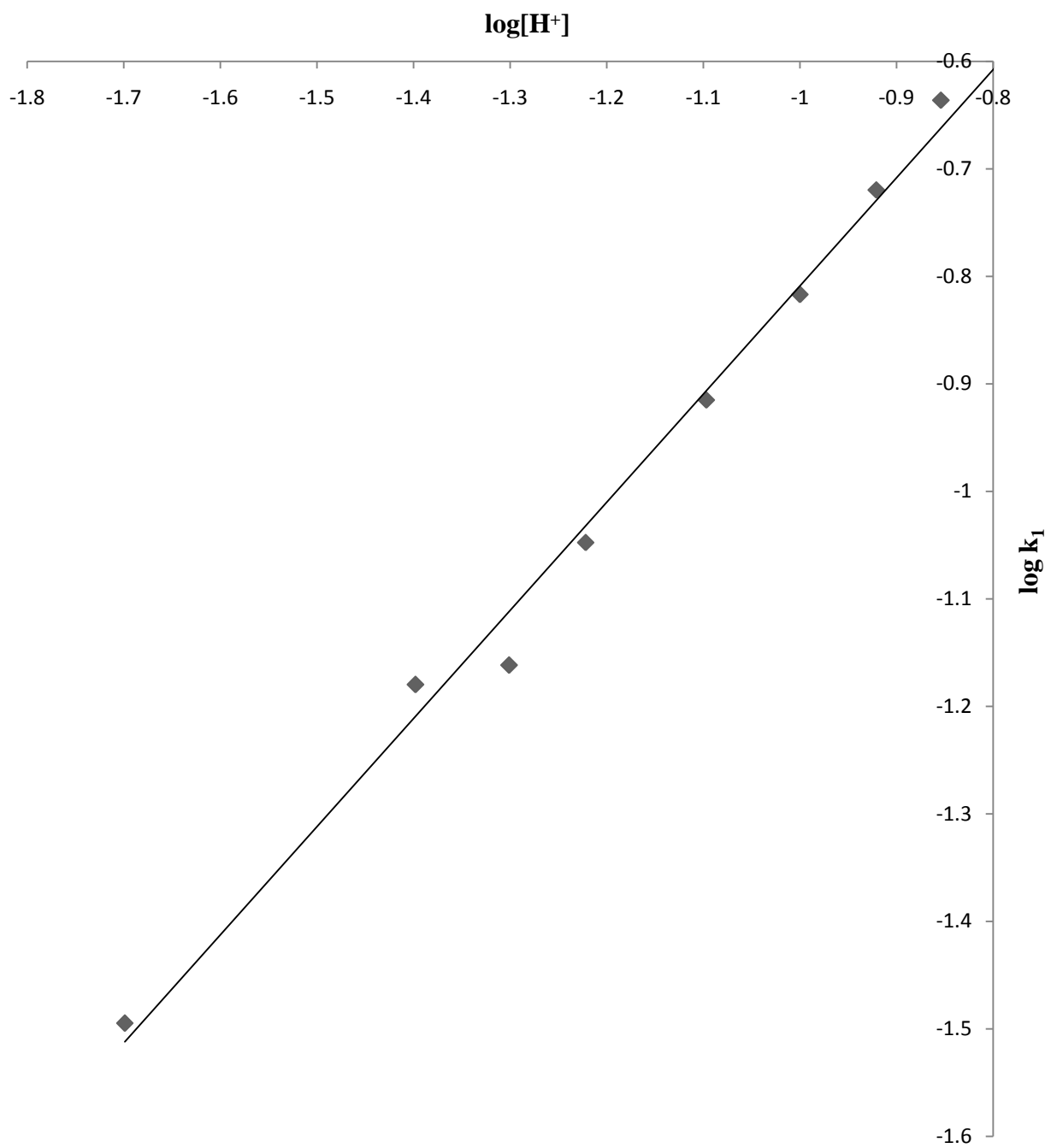


Figure 4.17: Plot of  $\log k_1$  versus  $\log [H^+]$  for the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

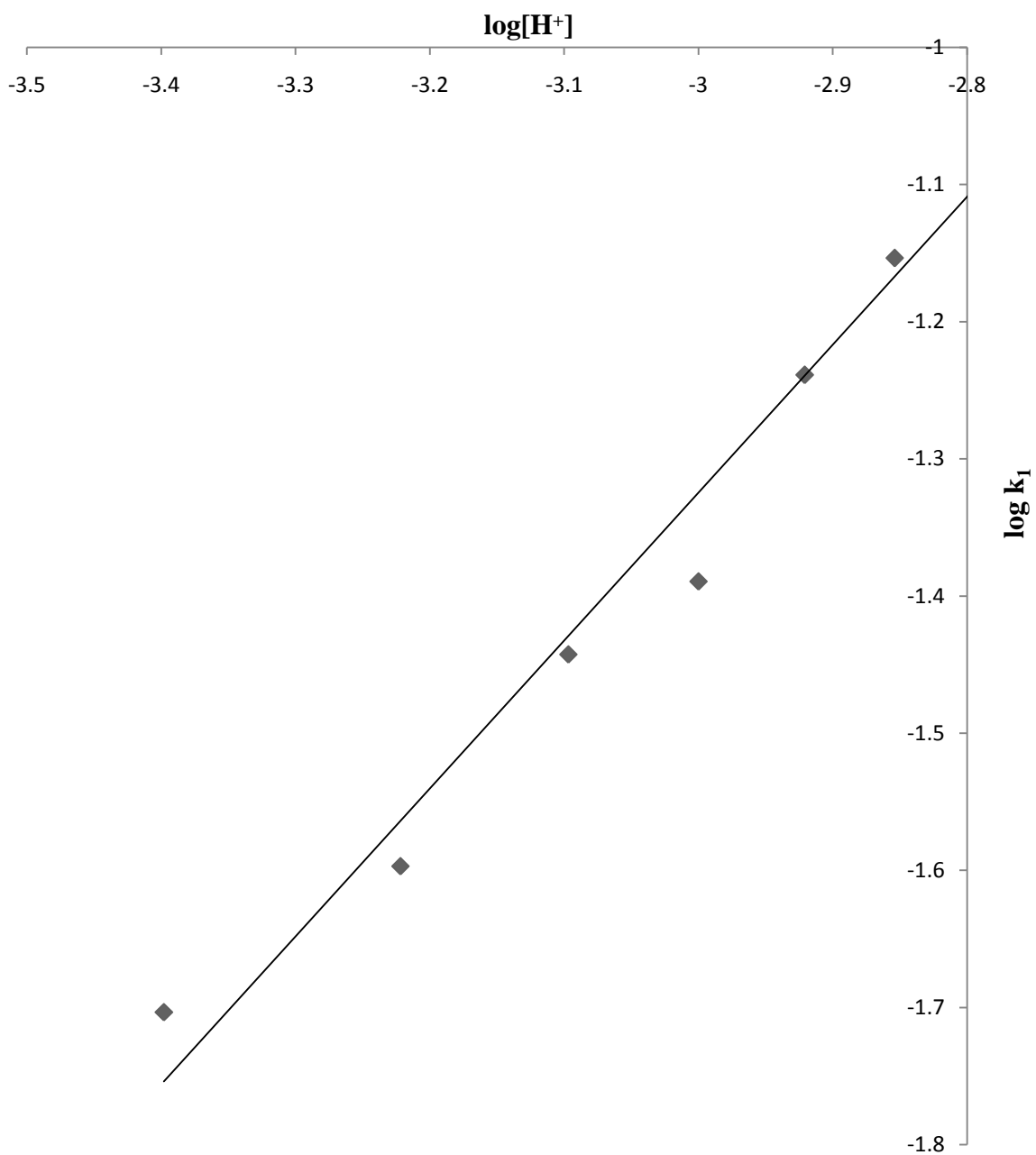


Figure 4.18: Plot of  $\log k_1$  versus  $\log [H^+]$  for the redox reaction of crystal violet with hypochlorite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

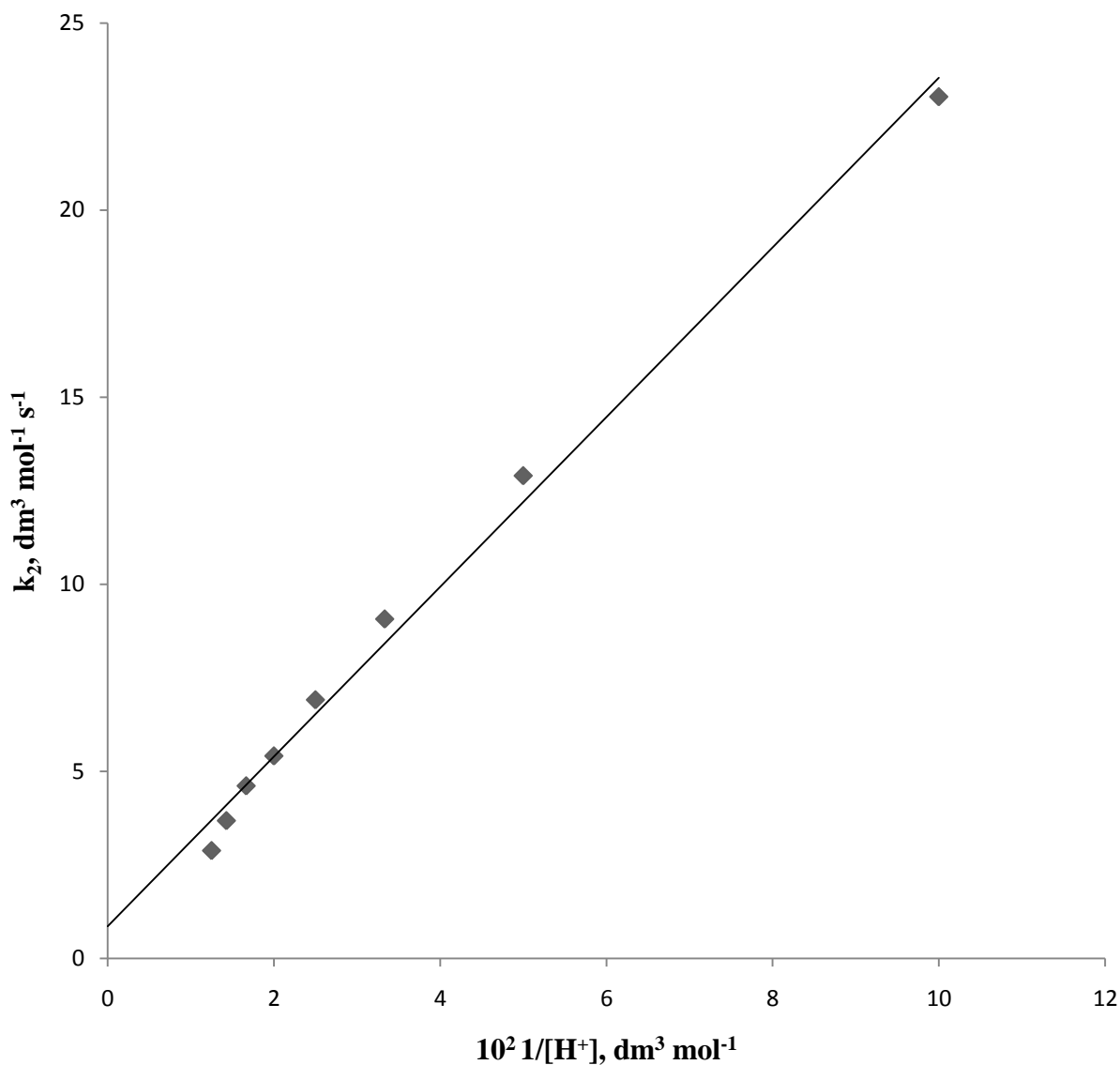


Figure 4.19: Plot of  $k_2$  versus  $1/[H^+]$  for the redox reaction of crystal violet with metabisulphite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

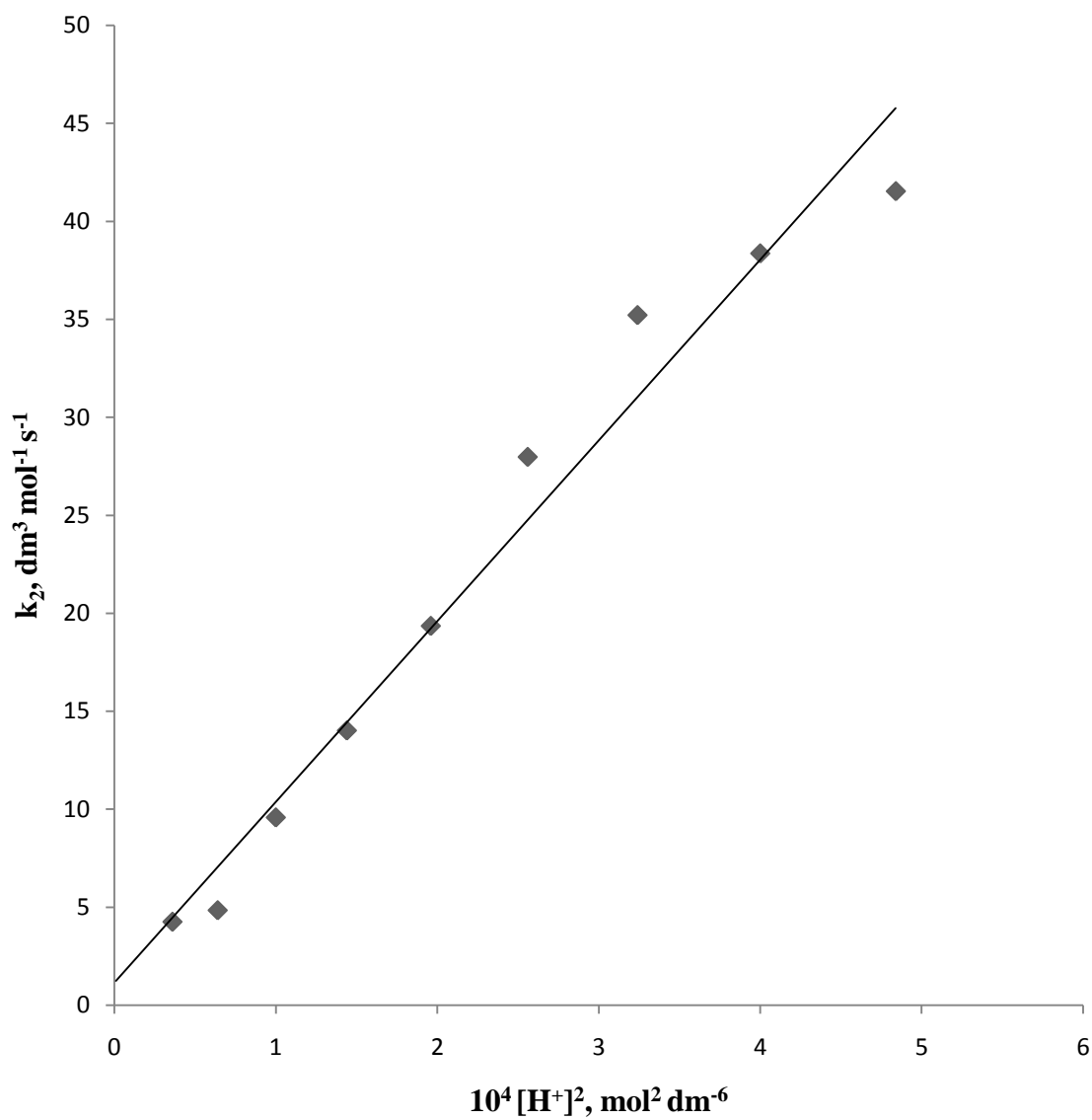


Figure 4.20: Plot of  $k_2$  versus  $[H^+]^2$  for the redoxreaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

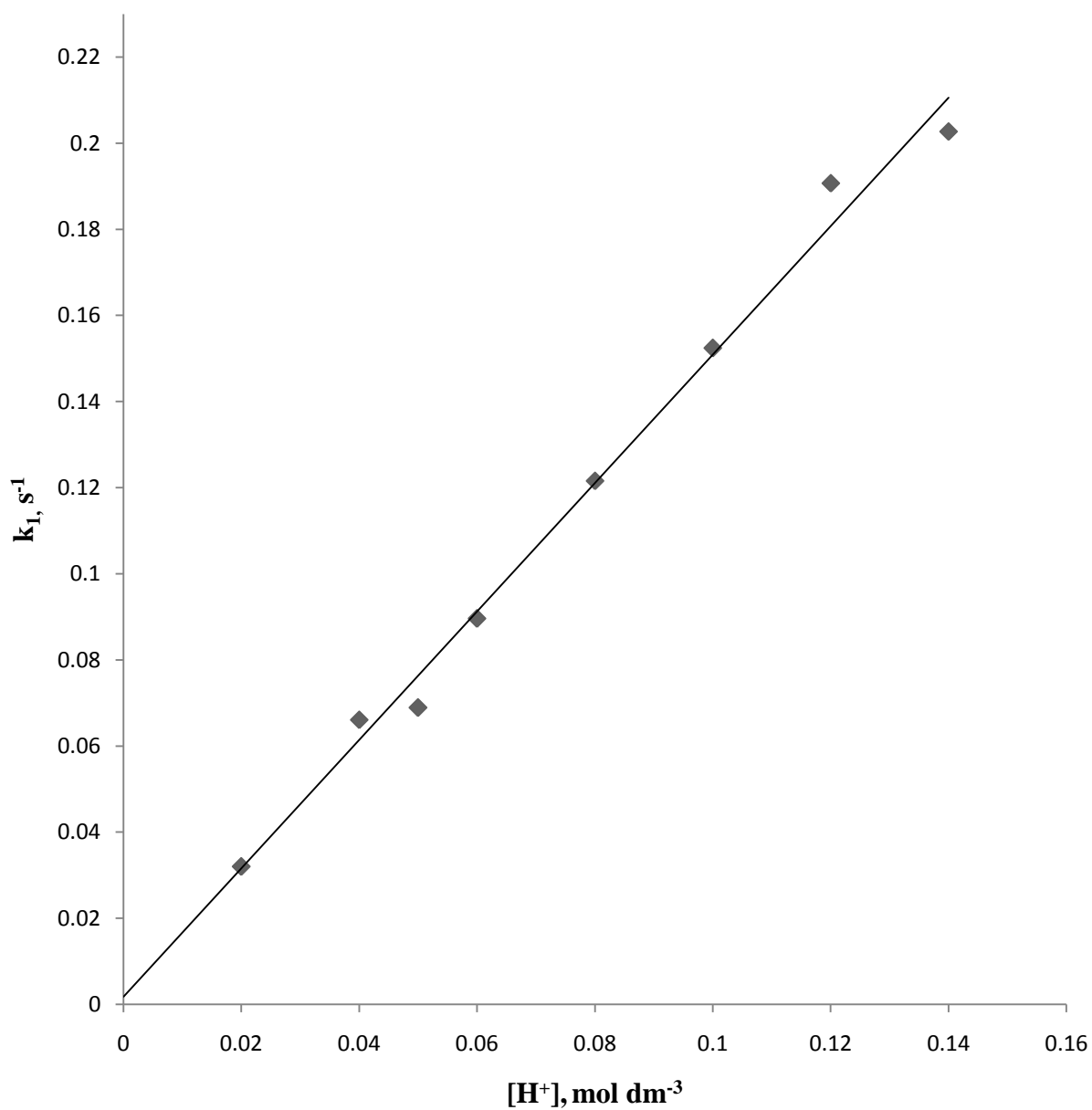
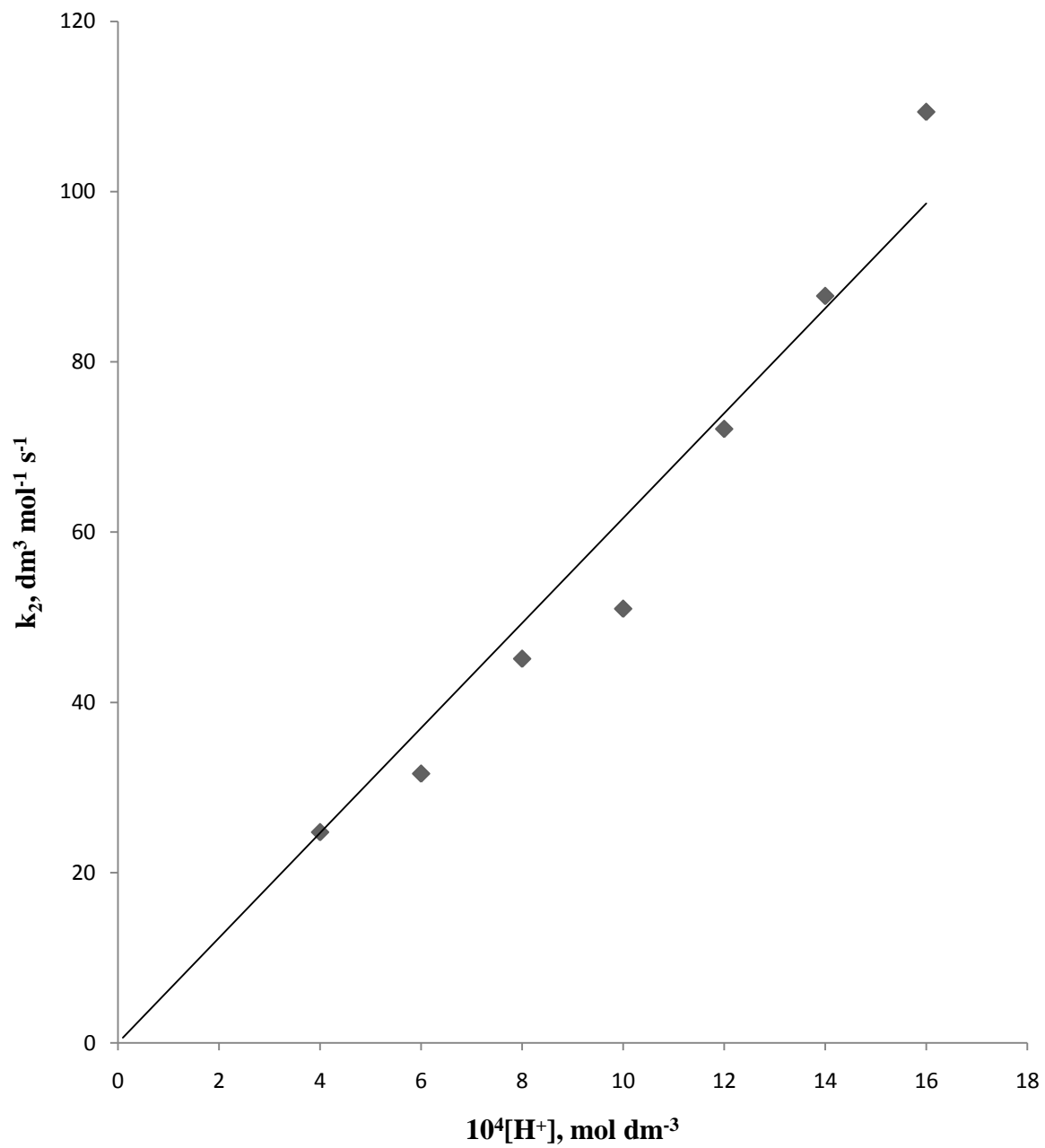


Figure 4.21: Plot of  $k_1$  versus  $[H^+]$  for the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol}$

$\text{dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.22:** Plot of  $k_2$  versus  $[H^+]$  for the redox reaction of crystal violet with hypochlorite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

where  $a = 2.27 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 0.86 \text{ s}^{-1}$ ,  $c = 9.22 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $d = 1.16 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$ ,

$e = 1.49 \text{ s}^{-1}$ ,  $f = 1.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $g = 6.16 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ .

The overall rate equations for the various systems are represented in equations (4.11-4.14).

$$\frac{-d[CV^+]}{dt} = (a + b [H^+]^{-1})[CV^+][S_2O_5^{2-}] \quad (4.11)$$

$$\frac{-d[CV^+]}{dt} = (c + d [H^+]^2)[CV^+][BrO_3^-] \quad (4.12)$$

$$\frac{-d[CV^+]}{dt} = (e + f [H^+])[CV^+] \quad (4.13)$$

$$\frac{-d[CV^+]}{dt} = (g [H^+])[CV^+][ClO^-] \quad (4.14)$$

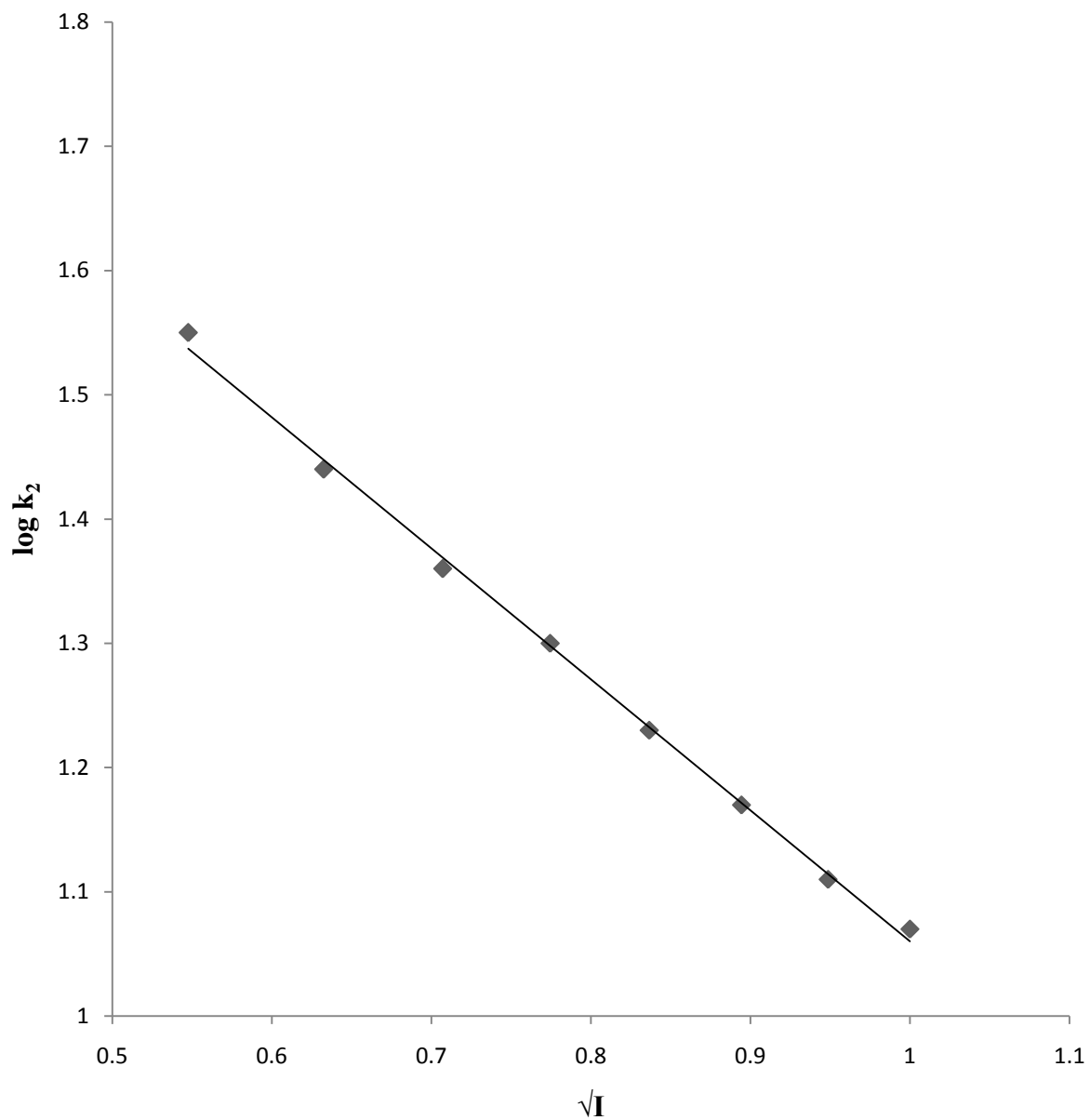
#### 4.4 Effect of ionic strength of the reaction medium on the reaction rate

The effect of changes in the ionic strength ( $I$ ) of the reaction medium was investigated in the range  $0.2\text{-}0.9 \text{ mol dm}^{-3}$  using  $NaClO_4$  for  $CV^+ - ClO^-$  system and  $NaCl$  for the rest of the

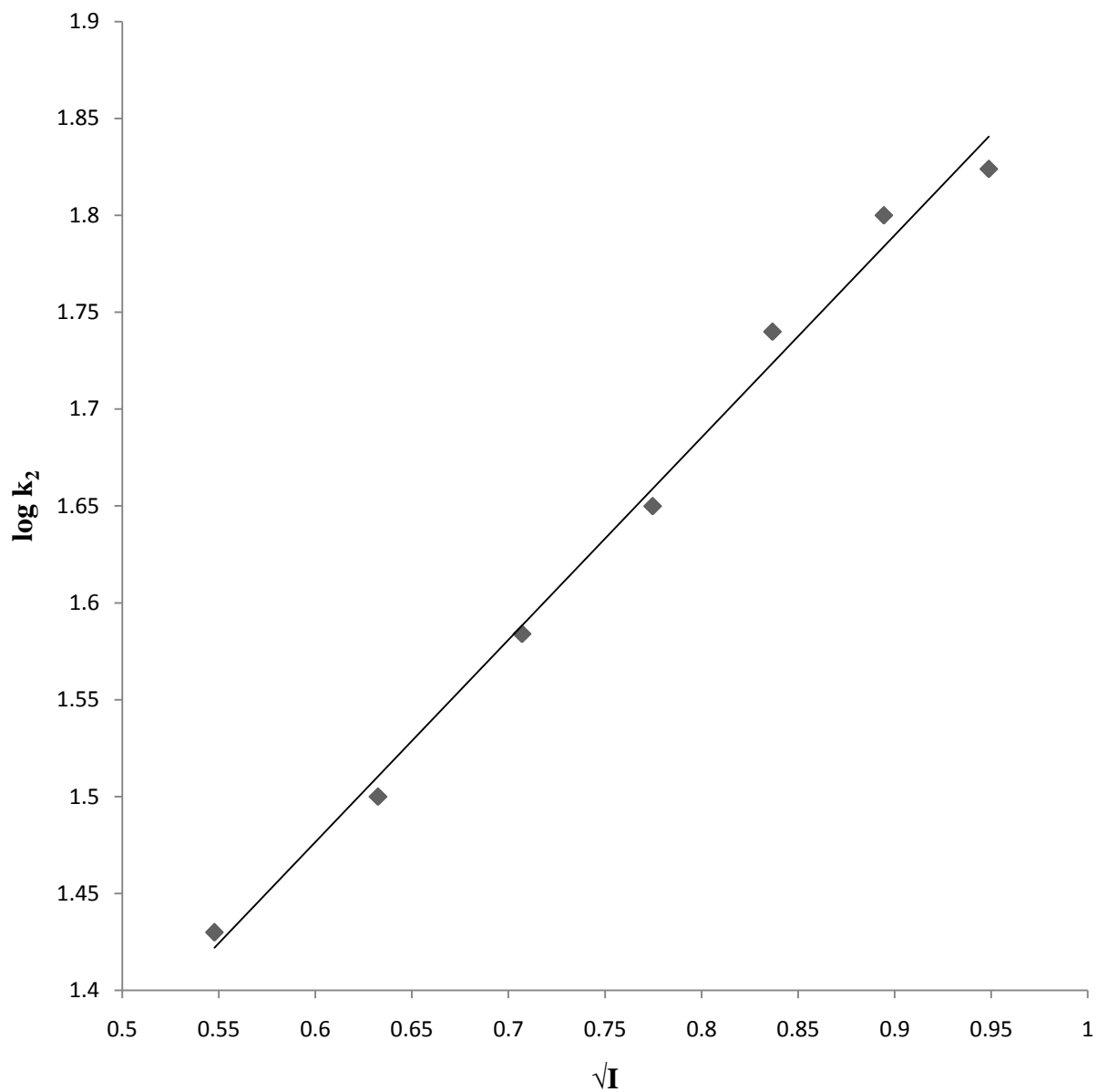


systems. The concentrations of other reactants were kept constant. The rates of the reactions were found to increase with increase in ionic strength of the reaction medium for the bromate and periodate ion systems, suggesting positive Bronsted-Debye salt effect. In the case of metabisulphite ion, the rate of the reaction decrease with increase in ionic strength of the reaction medium, while increase in ionic strength was found not to affect the reaction medium in the hypochlorite ion systems. The results are presented in Table (4.1-4.4).

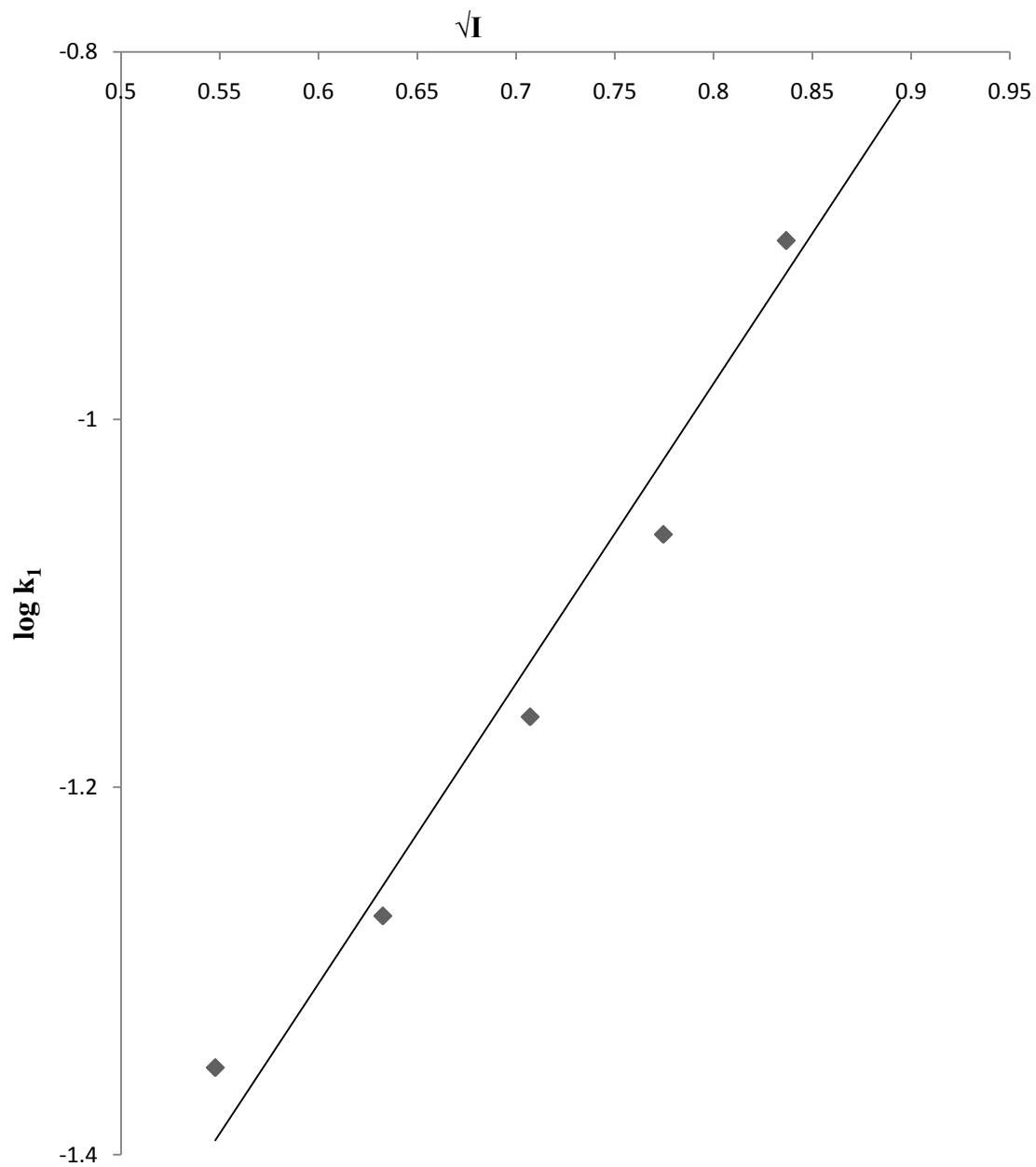
The logarithmic plots of  $k_2$  against  $\sqrt{I}$  are presented in Figures (4.23-4.25).



**Figure 4.23:** Plot of  $\log k_2$  versus  $\sqrt{I}$  for the redox reaction of crystal violet with metabisulphite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.24:** Plot of  $\log k_2$  versus  $\sqrt{I}$  for the redox reaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[BrO_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.25:** Plot of  $\log k_1$  versus  $\sqrt{I}$  for the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

#### **4.5 Effect of changes in dielectric constant of the reaction medium on the reaction rate**

The dielectric constant of the reaction medium was varied by addition of acetone to the reaction mixture; the corresponding effect of this on the rate of the reaction was studied. From the result, Table 4.5, the rate of the reaction decreased with increase in the amount of added acetone for the crystal violet- bromate ion system, but this has no effect on the rates of crystal violet metabisulphite ion, crystal violet periodate ion and crystal violet hypochlorite ion systems. Plot of dielectric constant dependent rate constant against  $1/D$  for the crystal violet-bromate ion system is presented in Figure 4.26.

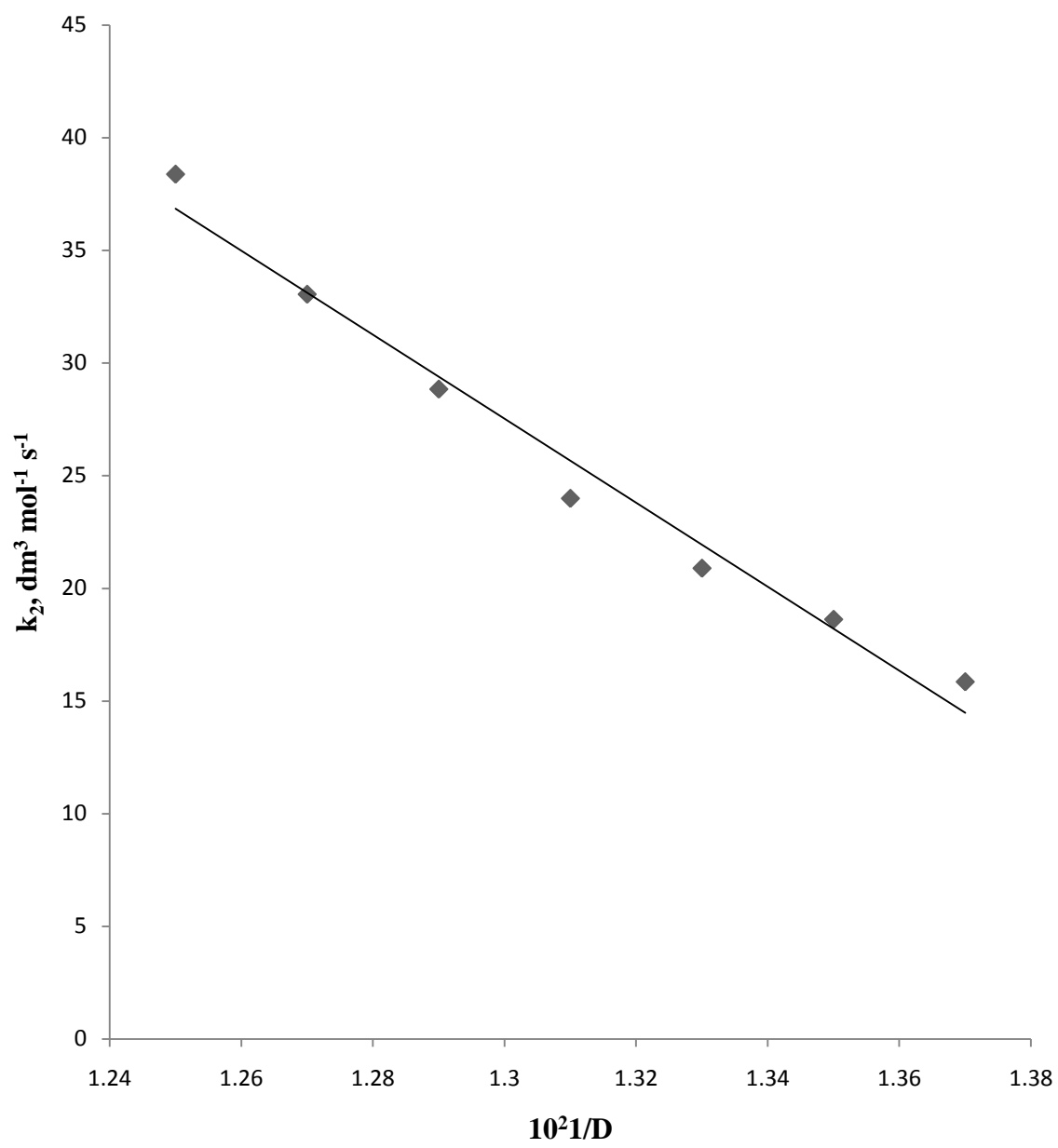
#### **4.6 Effect of added ions on the reaction rate**

The results of the effects of added anions on the rate of reaction, which was studied by keeping all other parameters constant and introducing varied concentrations of  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  showed that the rate of reactions decreased with increase in the anion concentration for  $\text{CV}^+ - \text{S}_2\text{O}_5^{2-}$  and  $\text{CV}^+ - \text{BrO}_3^-$  system, increased with increased in the anion concentration for  $\text{CV}^+ - \text{ClO}^-$  system, while increase in anion concentration had no effect on the rate of reaction for  $\text{CV}^+ - \text{IO}_4^-$  system. These are presented in Tables (4.6-4.9). The anion dependent rate constants against anion concentrations are presented in Figures (4.27-4.32).

For the effect of added cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were used for these investigations. Increase in the cation concentration inhibited the rate of reaction for  $\text{CV}^+-\text{BrO}_3^-$ , while for  $\text{CV}^+-\text{S}_2\text{O}_5^{2-}$ ,  $\text{CV}^+-\text{IO}_4^-$  and  $\text{CV}^+-\text{ClO}^-$  systems, increase in cation concentrations had no effect on the rate of reaction. These are presented in Tables (4.10-4.13). Plots of cations

**Table 4.5:** Pseudo-first order and second order rate constants for the effect of changes in dielectric constant of the medium on the redox reaction of crystal violet with bromate ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

D	$10^2 1/D$	$k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
80.10	1.25	0.3070	38.38
78.92	1.27	0.2649	33.05
77.74	1.29	0.2307	28.84
76.55	1.31	0.1919	23.99
75.37	1.33	0.1671	20.89
74.19	1.35	1.1489	18.62
73.01	1.37	0.1268	15.85



**Figure 4.26:** Plot of  $k_2$  against  $1/D$  for the redox reaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

**Table 4.6:** Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of crystal violet with metabisulphite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

X	$10^3[X], \text{ mol dm}^{-3}$	$k_1, \text{ s}^{-1}$	$k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
HCOO <sup>-</sup>	0	0.2303	23.03
	10	0.2198	21.98
	20	0.1936	19.36
	40	0.1852	18.52
	60	0.1694	16.94
	80	0.1607	16.07
	100	0.1553	15.53
CH <sub>3</sub> COO <sup>-</sup>	0	0.2303	23.03
	10	0.2265	22.65



20	0.2107	21.07
40	0.2034	20.34
60	0.1922	19.22
80	0.1834	18.34
100	0.1715	17.15

**Table 4.7:** Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[BrO_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

X	$10^3[X], \text{ mol dm}^{-3}$	$k_1, \text{ s}^{-1}$	$k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
HCOO <sup>-</sup>	0	0.3070	38.38
	10	0.2811	35.14
	20	0.2672	33.40

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	40	0.2501	31.26
	60	0.2352	29.40
	80	0.2113	26.41
	100	0.1902	23.78
CH <sub>3</sub> COO <sup>-</sup>	0	0.3070	38.38
	10	0.3070	38.38
	20	0.2904	36.30
	40	0.2844	35.55
	60	0.2773	34.66
	80	0.2568	32.10
	100	0.2435	30.44

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**Table 4.8:** Pseudo-first order rate constants for the effect of added anions on the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm$

1 °C

X	$10^3[X], \text{ mol dm}^{-3}$	$10^2k_1, \text{ s}^{-1}$
HCOO <sup>-</sup>	0	6.89
	10	6.64
	20	6.46
	40	6.44
	60	6.87
	80	6.96
	100	6.61
CH <sub>3</sub> COO <sup>-</sup>	0	6.89
	10	6.88
	20	6.62
	40	6.05
	60	6.76
	80	6.91
	100	6.34

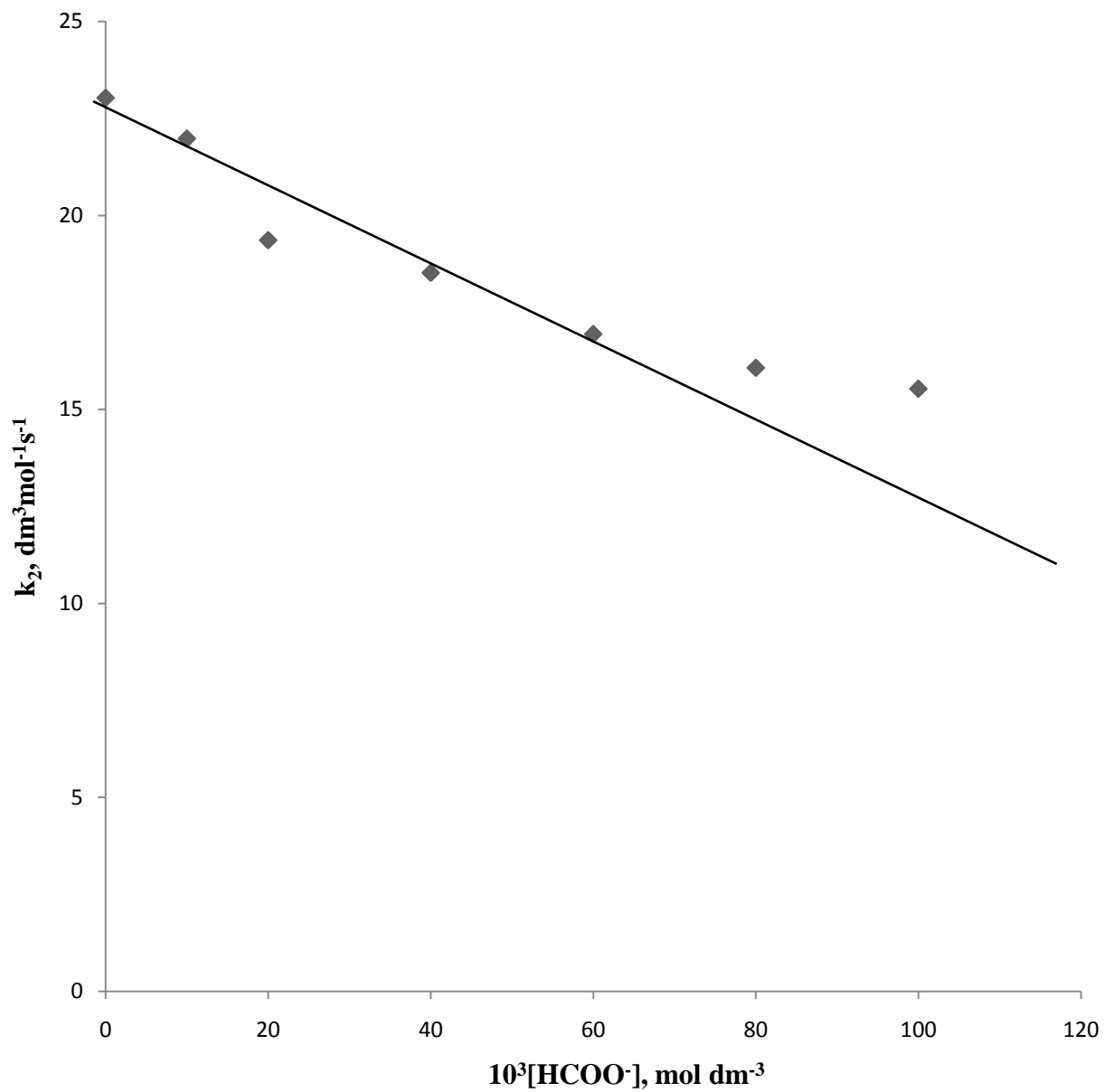
**Table 4.9:** Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of crystal violet with hypochlorite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

X	$10^3[X], \text{ mol dm}^{-3}$	$10^2 k_1, \text{ s}^{-1}$	$k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
HCOO <sup>-</sup>	0	4.08	51.00
	10	5.21	65.13
	20	7.08	88.50
	40	8.21	102.63
	60	9.42	117.75
	80	11.02	137.75
	100	11.94	149.25
CH <sub>3</sub> COO <sup>-</sup>	0	4.08	51.00

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10	4.82	60.25
20	5.57	69.63
40	6.82	85.25
60	8.21	102.63
80	9.88	123.50
100	10.75	134.38

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**Figure 4.27:** Plot of  $k_2$  versus  $[\text{HCOO}^-]$  for the redox reaction crystal violet with metabisulphite ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

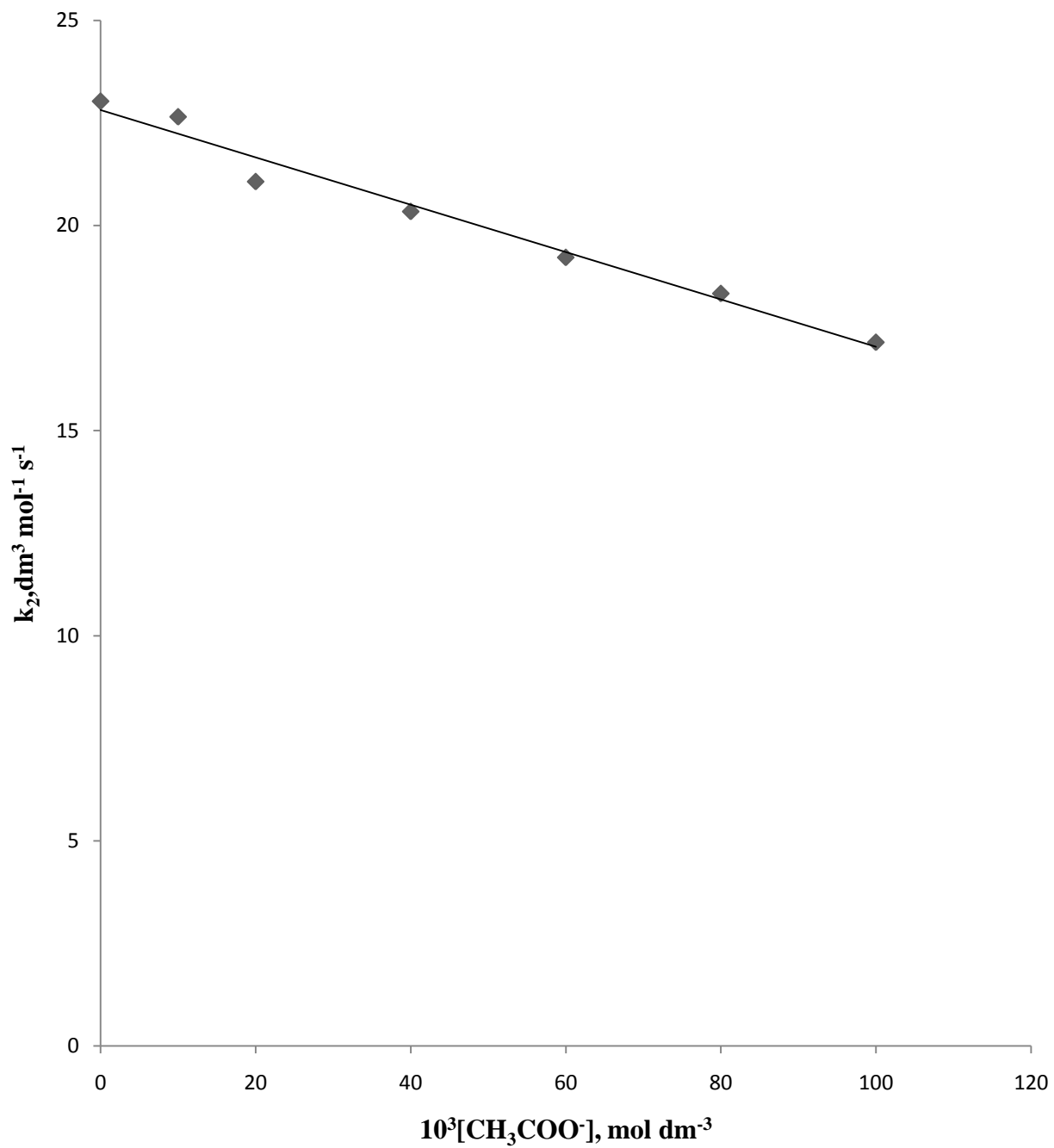
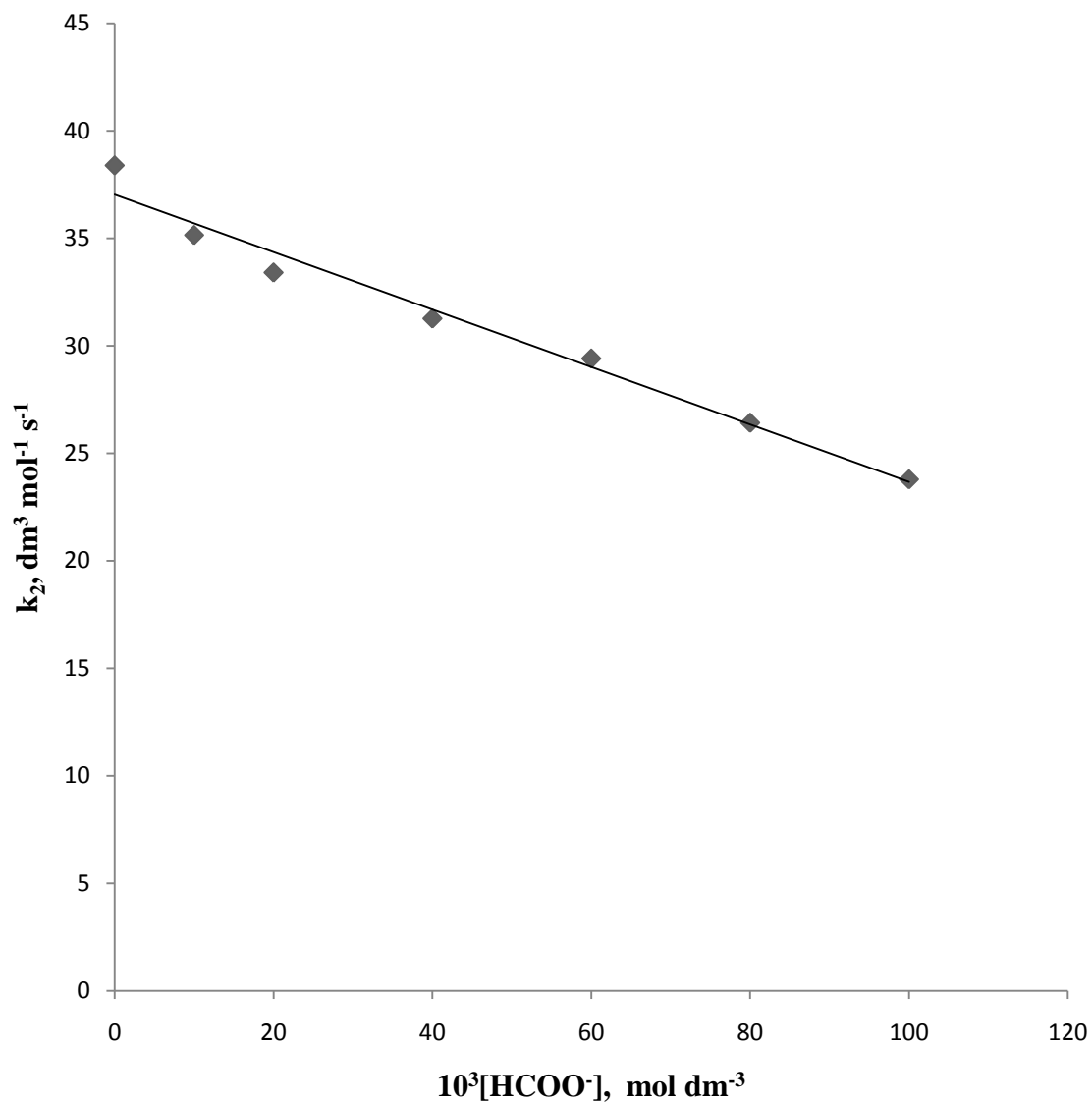
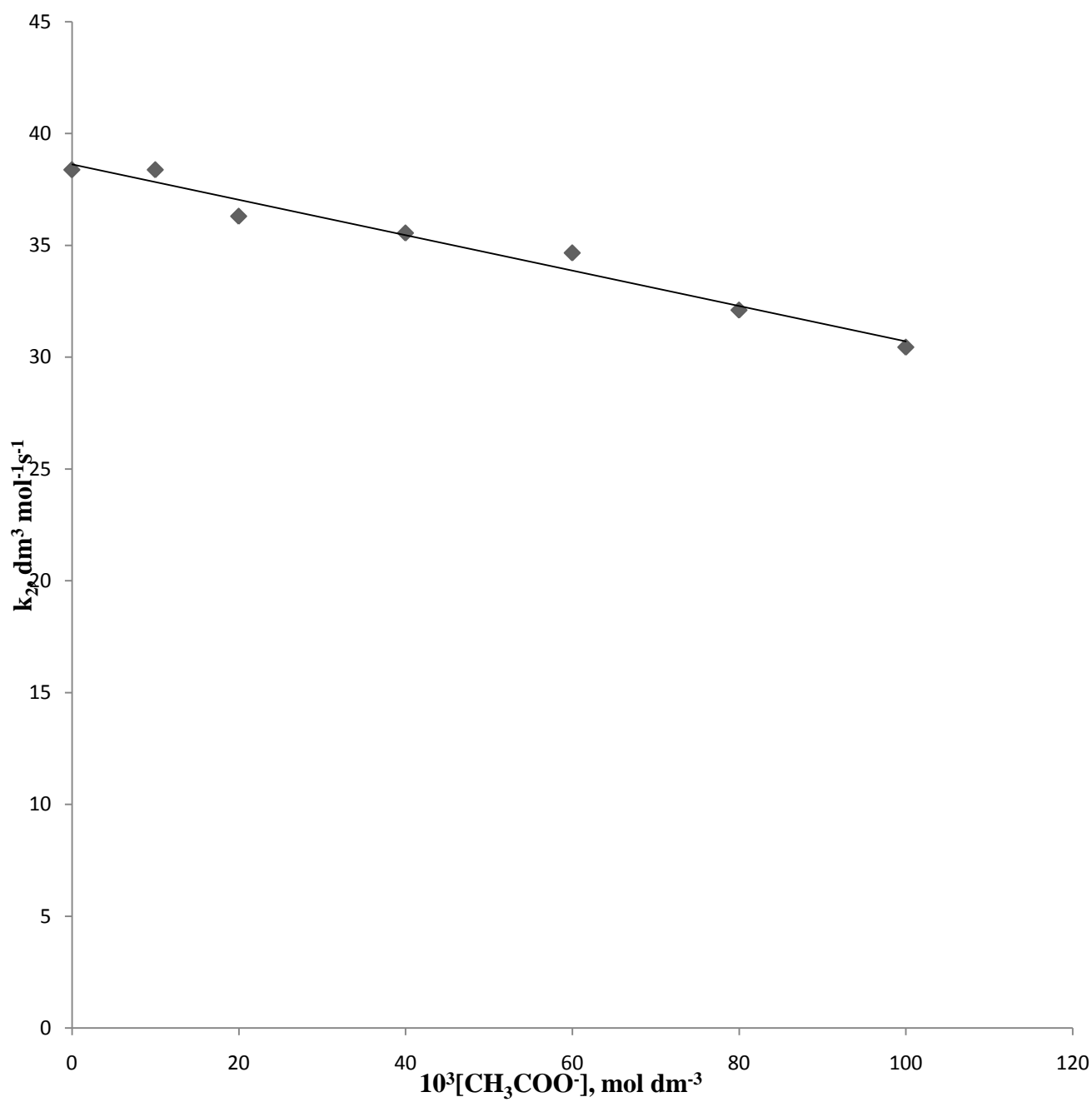


Figure 4.28: Plot of  $k_2$  versus  $[\text{CH}_3\text{COO}^-]$  for the redox reaction crystal violet with metabisulphite ion at  $\text{CV}^+ = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

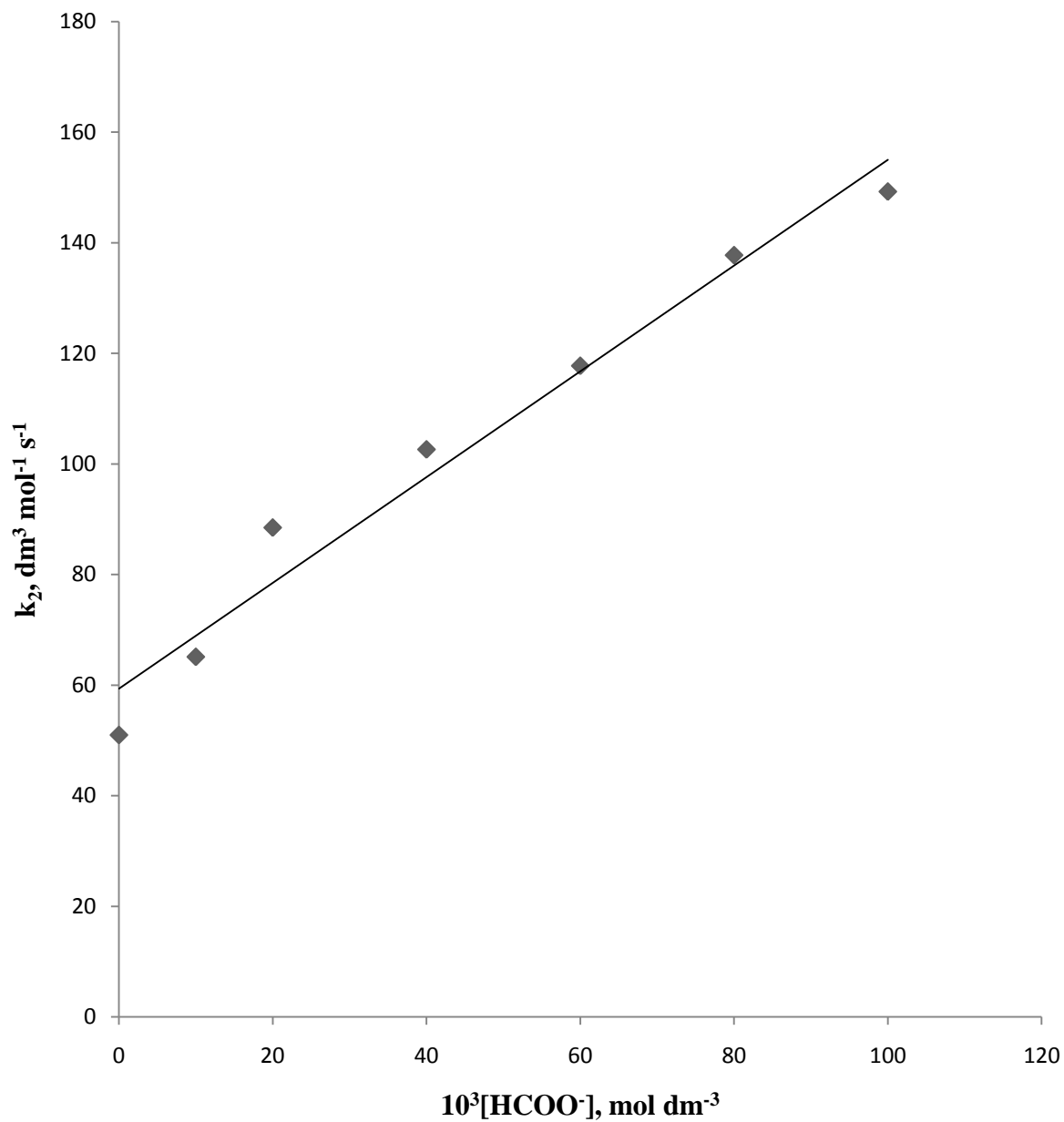


**Figure 4.29:** Plot of  $k_2$  versus  $[\text{HCOO}^-]$  for the redox reaction crystal violet with bromate ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

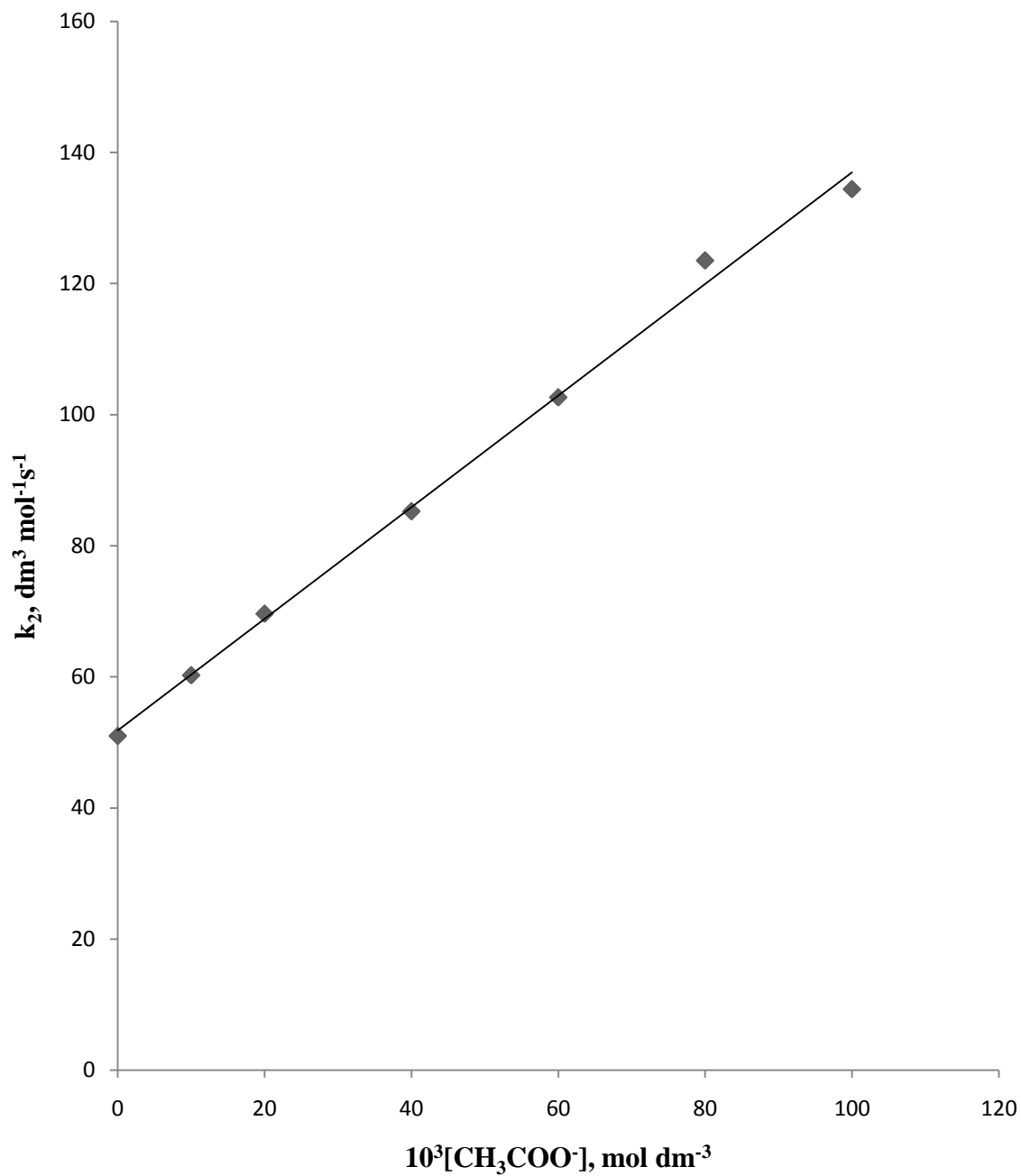




**Figure 4.30:** Plot of  $k_2$  versus  $[\text{CH}_3\text{COO}^-]$  for the redox reaction crystal violet with bromate ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.31:** Plot of  $k_2$  versus  $[\text{HCOO}^-]$  for the redox reaction crystal violet with hypochlorite ion at  $[\text{CV}^+]=1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-]=8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I=0.50 \text{ mol dm}^{-3}$  and  $T=28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.32:** Plot of  $k_2$  versus  $[\text{CH}_3\text{COO}^-]$  for the redox reaction crystal violet with hypochlorite ion at  $\text{CV}^+ = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

**Table 4.10:** Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with metabisulphite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

X	$10^3[X], \text{ mol dm}^{-3}$	$k_1, \text{ s}^{-1}$	$k_2, \text{ mol dm}^{-3}$
$\text{Ca}^{2+}$	0	0.2303	23.03
	10	0.2284	22.84
	20	0.2310	23.10
	40	0.2302	23.02
	80	0.2303	23.03
	100	0.2287	22.87
$\text{Mg}^{2+}$	0	0.2298	22.98
	10	0.2303	23.03
	20	0.2313	23.13
	40	0.2291	22.91
	80	0.2306	23.06
	100	0.2303	23.03

**Table 4.11:** Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

X	$10^3[X], \text{ mol dm}^{-3}$	$k_1, \text{ s}^{-1}$	$k_2, \text{ mol}^{-1}\text{dm}^{-3}$
$\text{Ca}^{2+}$	0	0.3070	38.38
	10	0.2967	37.09
	20	0.2901	36.26
	40	0.2845	35.56
	80	0.2772	34.65
	100	0.2700	33.75
$\text{Mg}^{2+}$	0	0.3070	38.38
	10	0.2868	35.85
	20	0.2560	32.00

40	0.2432	30.40
80	0.2316	28.95
100	0.2213	27.66

**Table 4.12:** Pseudo-first order rate constant for the effect of added cations on the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm$

**1 °C**

X	$10^3[X], \text{ mol dm}^{-3}$	$10^2 k_1, \text{ s}^{-1}$
Ca <sup>2+</sup>	0	6.61
	10	6.52
	20	6.58

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	40	6.65
	80	6.61
	100	6.66
Mg <sup>2+</sup>	0	6.61
	10	6.67
	20	6.72
	40	6.55
	80	6.61
	100	6.61

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**Table 4.13:** Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of crystal violet with hypochlorite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

X	$10^3[X], \text{ mol dm}^{-3}$	$10^2k_1, \text{ s}^{-1}$	$k_2, \text{ mol dm}^{-3}$
$Ca^{2+}$	0	4.08	51
	10	3.97	49.63
	20	4.02	50.25
	40	4.21	52.63
	80	4.12	51.5
	100	3.82	47.75
$Mg^{2+}$	0	3.82	47.75
	10	4.03	50.38
	20	4.08	51.00
	40	4.34	54.25
	80	4.26	53.25
	100	4.14	51.75



dependent rate constants against cations concentrations are presented in Figures (4.33-4.34).

#### **4.7 Test for intermediate complex**

##### **4.7.1 Test for free radicals**

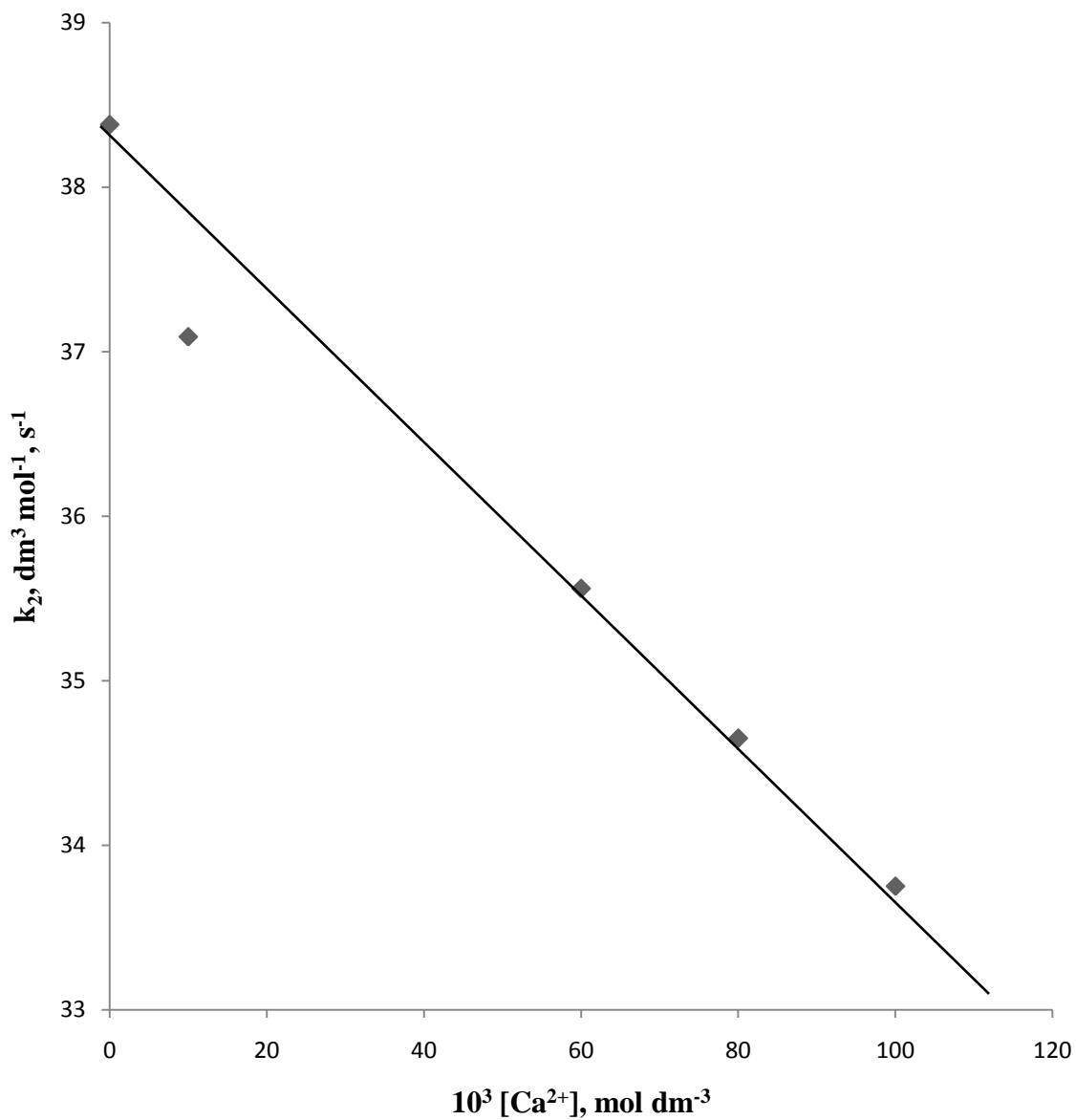
Acrylamide was added to the partially oxidized reaction mixtures and to the reactants separately to initiate free radical polymerization. For all the systems investigated, there was no formation of gelatinous precipitate which indicates the absence of free radical in the reaction mixtures.

##### **4.7.2 Michaelis-Menten plot**

The Michaelis-Menten plot  $1/k_1$  versus  $1/[\text{oxyanions}]$ , were all linear for all the systems and passed through the origin (Figures 4.35-4.37). These observations suggest the absence of intermediate complex formation prior to the rate determining step.

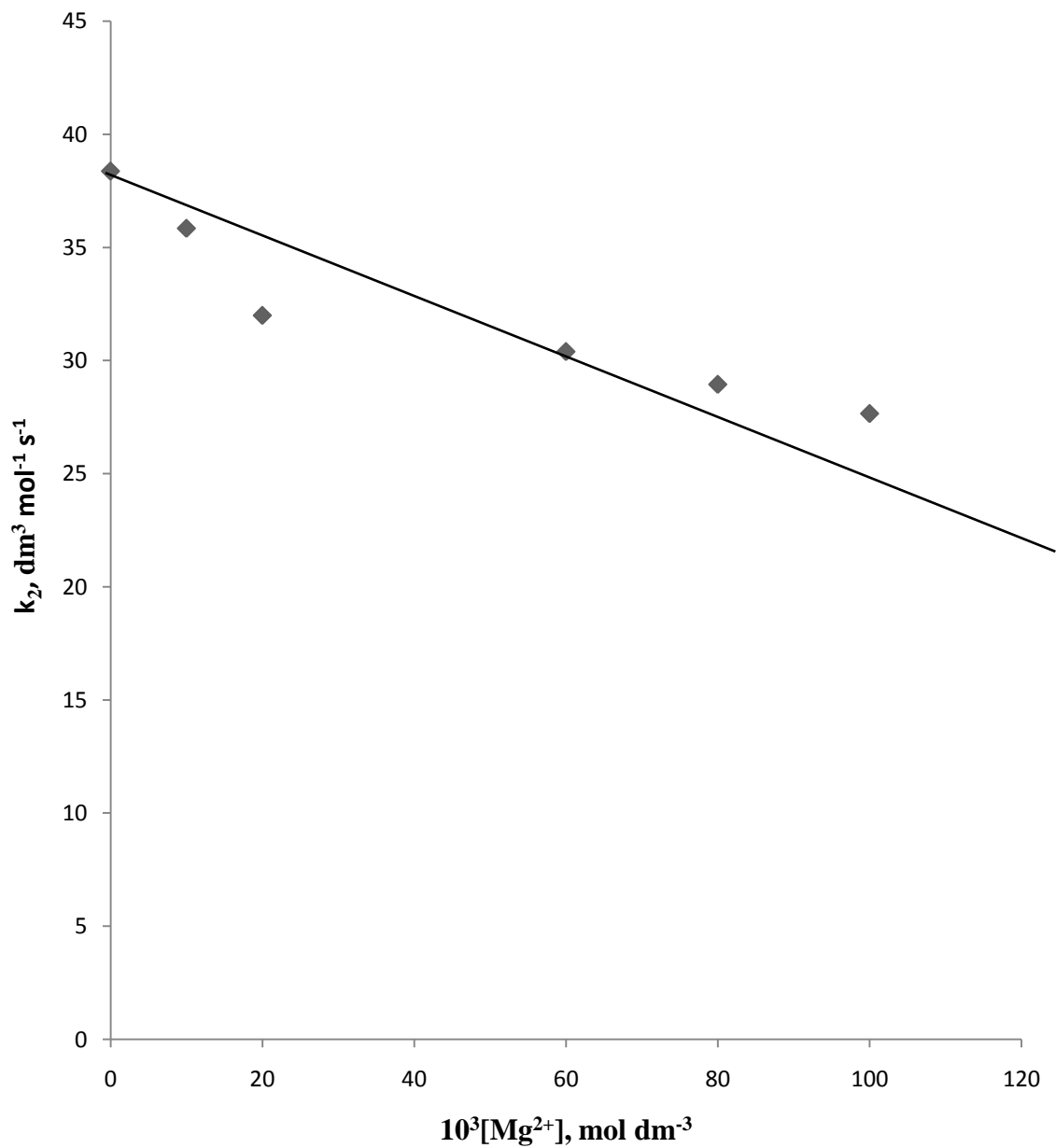
##### **4.7.3 Spectrophotometric test**

Spectrophotometric test was carried out to detect the presence of any intermediate complex of significant stability in the reactions. These tests were performed by comparing the electronic spectra of the reaction mixtures taken after two or five minutes of the commencement of the reactions, with that of crystal violet solution within the wavelength range of 500-700 nm to check for any appearance of new peak or shift in the  $\lambda_{\max}$  of 585nm characteristic of crystal violet. For all the systems studied except for  $\text{CV}^+ - \text{IO}_4^-$ , where there is shift in the  $\lambda_{\max}$  from 585-620 nm, no new peak or shift in the  $\lambda_{\max}$  was observed. The spectra are shown in Figures (4.38-4.41).



**Figure 4.33:** Plot of  $k_2$  versus  $[\text{Ca}^{2+}]$  for the redox reaction crystal violet with bromate ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol}$

$\text{dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.34:** Plot of  $k_2$  versus  $[\text{Mg}^{2+}]$  for the redox reaction crystal violet with bromate ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

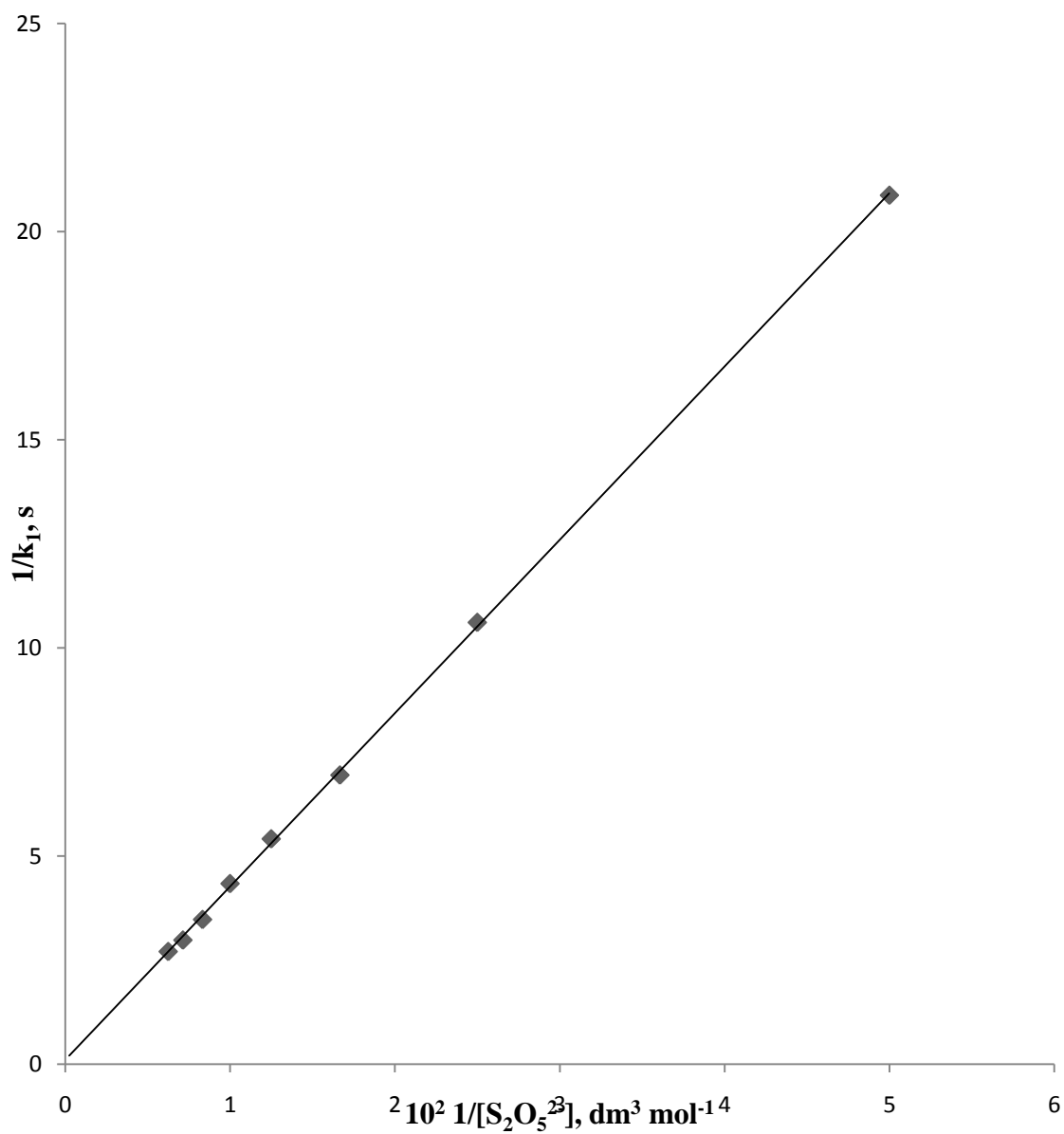
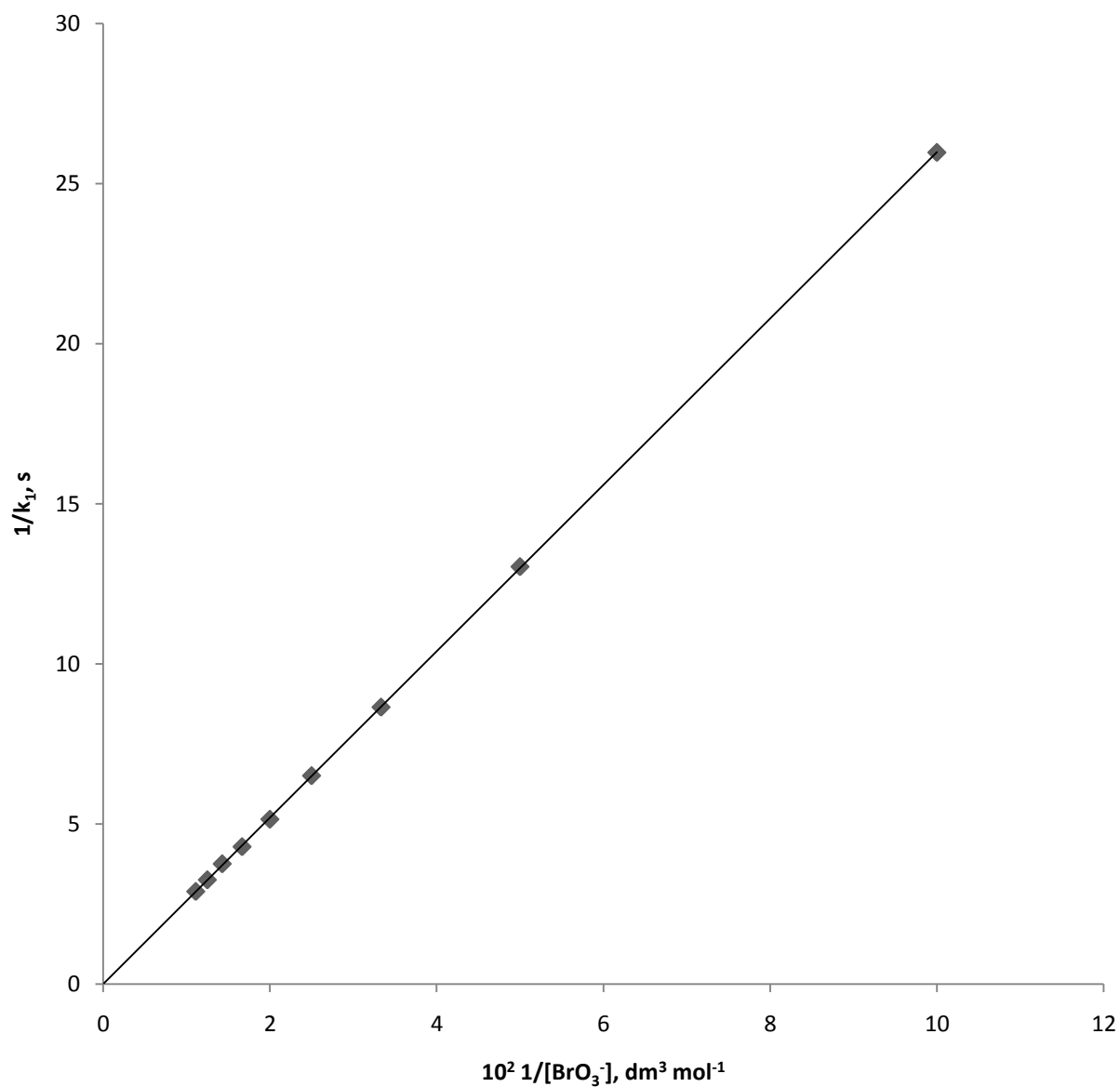
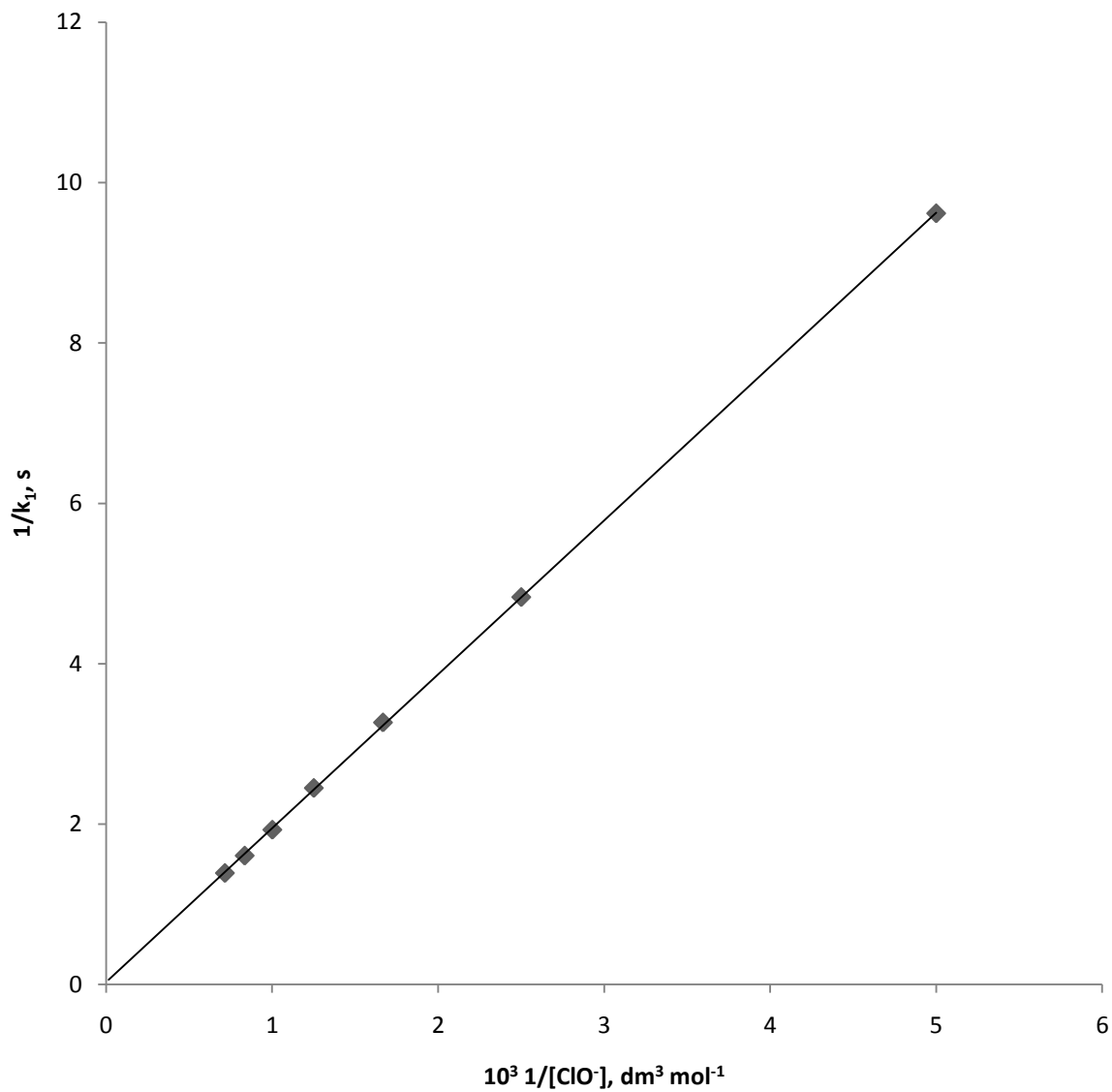


Figure 4.35: Michaelis-Menten plot of  $1/k_1$  versus  $1/[S_2O_5^{2-}]$  for the redox reaction of crystal violet with metabisulphite ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 30 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.36:** Michaelis-Menten plot of  $1/k_1$  versus  $1/[\text{BrO}_3^-]$  for the redox reaction of crystal violet with bromate ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Figure 4.37:** Michaelis-Menten plot of  $1/k_1$  versus  $1/[\text{ClO}^-]$  for the redox reaction of crystal violet with hypochlorite ion at  $[\text{CV}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

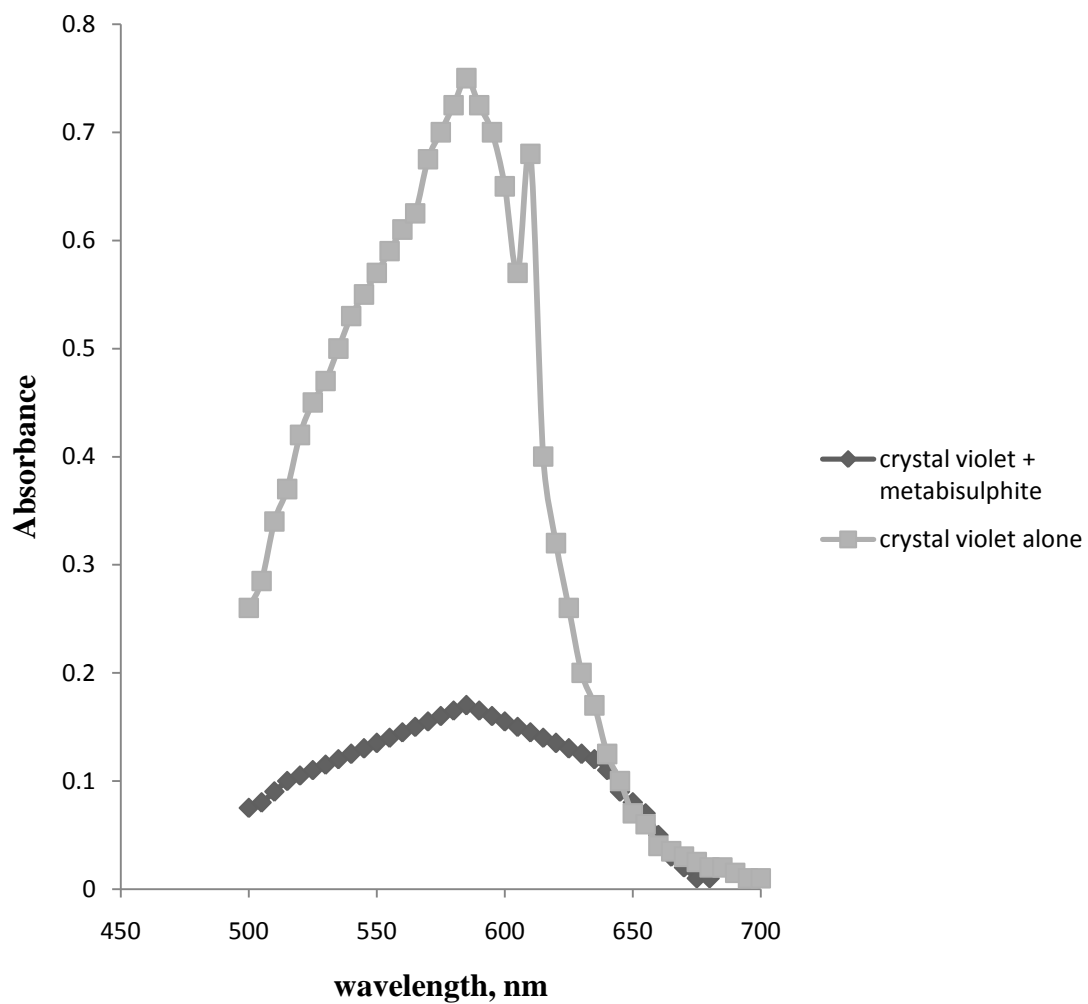


Figure 4.38: Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and metabisulphite ion at  $CV^+ = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_5^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = (500-700) \text{ nm}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



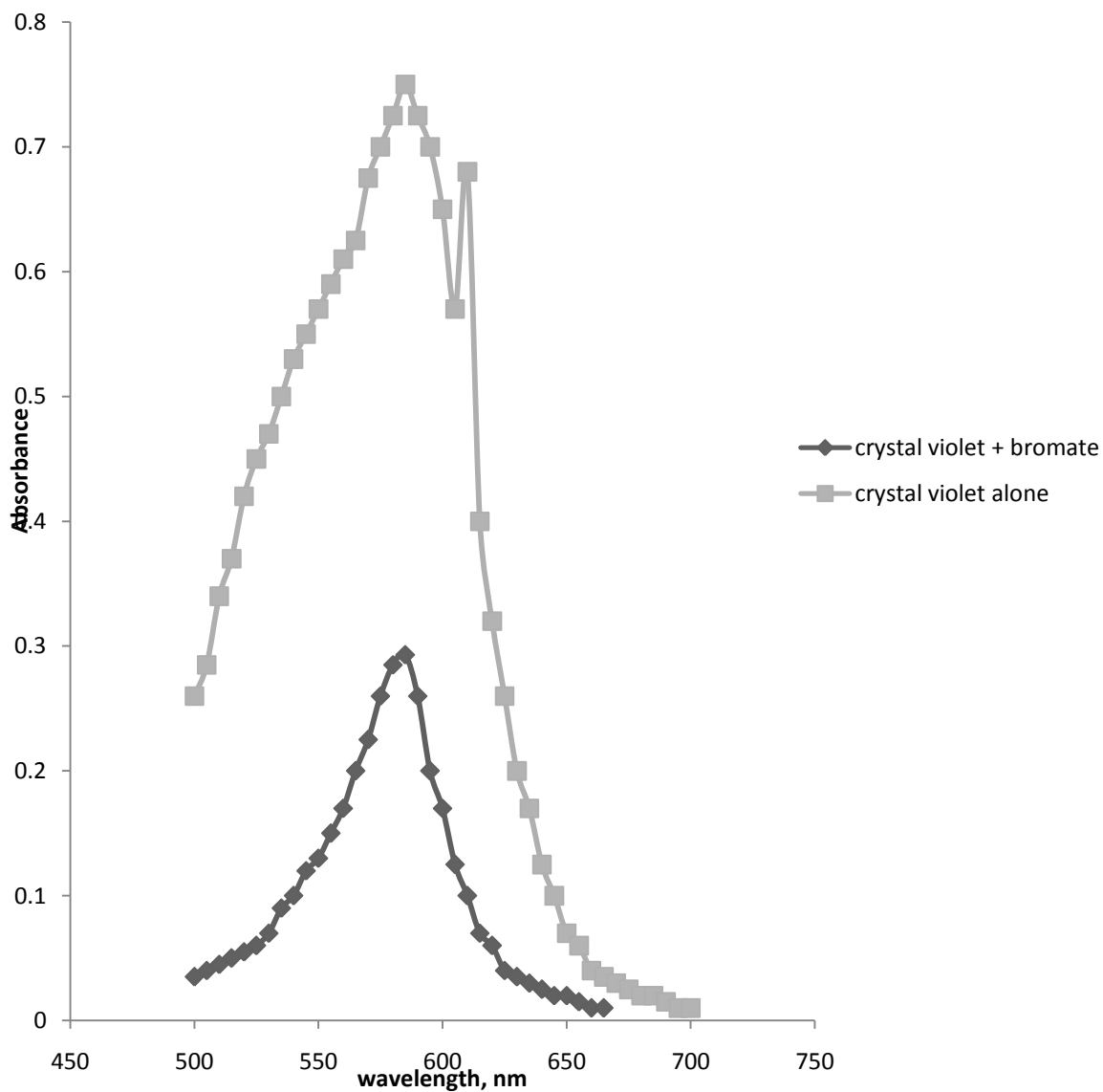


Figure 4.39: Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and bromate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[BrO_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,

$\lambda_{\text{max}} = (500-670) \text{ nm}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

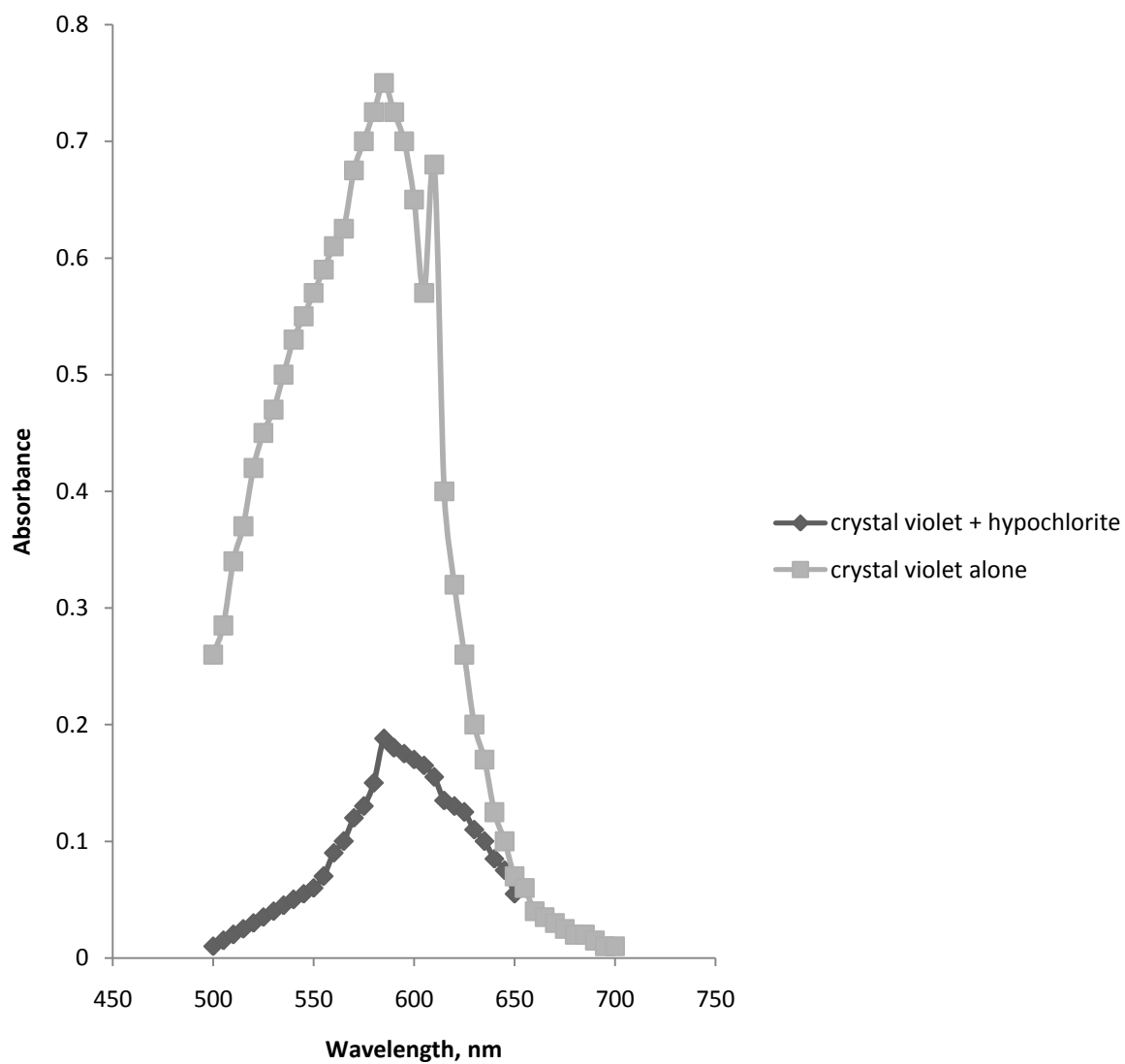
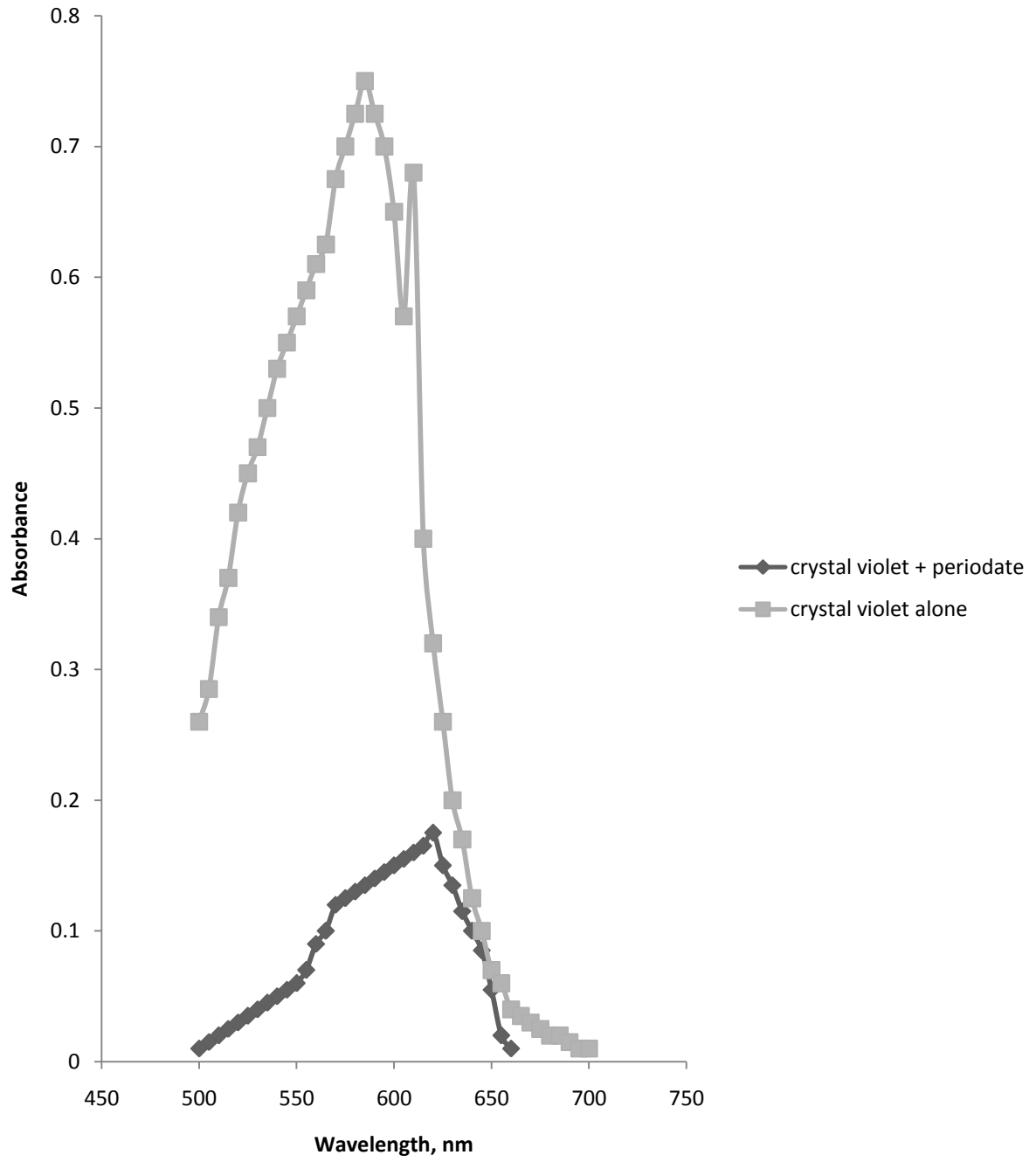


Figure 4.40: Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and hypochlorite ion at  $CV^+ = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO^-] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol}$

$\text{dm}^{-3}$ ,  $\lambda_{\text{max}} = (500-670) \text{ nm}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



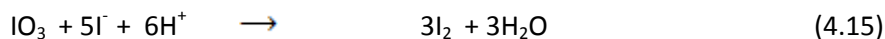
**Figure 4.41: Spectra of crystal violet and that of partially oxidized reaction mixture of crystal violet and hypochlorite ion at  $CV^+ = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol}$**

**$\text{dm}^{-3}$ ,  $\lambda_{\text{max}} = (500-670) \text{ nm}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$**

#### 4.8 Products Analysis

The products of these reactions were subjected to qualitative inorganic analyses. Bromine was confirmed as one of the product of  $CV^+-BrO_3^-$  reaction by addition of potassium bromide crystal followed by manganese dioxide and few drops concentrated sulphuric acid and warming gently. Formation of a reddish brown vapour with irritating smell and acidic to litmus paper confirmed the presence of bromine. For the  $CV^+-S_2O_5^{2-}$ , sulphate ion was confirmed by addition of  $BaCl_2$  solution followed by excess dilute HCl. Formation of white precipitate which was insoluble in excess dilute HCl confirmed the presence of  $SO_4^{2-}$  (Vogel, 1961). In the  $CV^+-ClO^-$  reaction,  $Cl^-$  was confirmed by addition of  $2 \text{ mol dm}^{-3} \text{ HNO}_3$  followed by few drops of  $AgNO_3$ . Formation of white precipitate which dissolves in  $2 \text{ mol dm}^{-3}$  ammonia confirmed the presence of  $Cl^-$  (Vogel, 1961).

Iodate ion, one of the products of  $CV^+-IO_4^-$  reaction was confirmed qualitatively through the positive starch-indicator test for liberated  $I_2$  when KI was added to the reaction mixture. The reaction of iodate by iodide ions in acidic medium liberates molecular iodine as given by the equation (Jeffery, 1991);



## CHAPTER FIVE

### 5.0 DISCUSSION

#### 5.1 Crystal violet- metabisulphite ion system

The results of the stoichiometric investigations indicated that one mole of crystal violet was consumed by one mole of metabisulphite. This agrees with the stoichiometries observed in the reactions of  $S_2O_5^{2-}$  with triphenylmethane dye (Onu and Iyun, 2001) and basic fuchsin (Lawal, 1997). However, stoichiometry of 1:3 was established for the reduction of methylene blue with metabisulphite (Babatunde *et al.*, 2013).

The order of the reaction was found to be one in both the oxidant and reductant respectively. Thus the reaction is second order overall and the second order rate constant  $k_2$  was determined to be  $k_2 = (23 \pm 0.45) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Similar order was obtained with respect to the reductant concentration by earlier workers (Gupta *et al.*, 1987, Lawal, 1997, Onu and Iyun 2001 and Babatunde *et al.*, 2013). The order of zero in the [reductant] was observed in the

reaction of  $\text{Fe}_2\text{O}^{4+}$  and  $\text{S}_2\text{O}_5^{2-}$  (Idris *et al.*, 2005), thus the  $k_1$  evaluated from the slopes of the pseudo-first order plots were constant irrespective of the concentration of  $\text{S}_2\text{O}_5^{2-}$ .

The studies on the effect of hydrogen ion concentration,  $[\text{H}^+]$ , on the rate of the reaction showed that increase in hydrogen ion concentration decreased the rate of reaction with negative slope of 0.97 (Figure 4.15). Least square plot of  $k_2$  versus  $[1/\text{H}^+]$  had intercept (Figure 4.19), this showed two parallel reaction pathways: the acid independent and the inverse acid dependent pathways. The inverse acid pathway shows that there is a pre-equilibrium step before the rate determining step in which a proton is lost. This means that the two rate-controlling steps are preceded by a rapid equilibrium for which the equilibrium constant is small, and both the forms, protonated and deprotonated, are reactive (Gupta and Gupta 1984). Similar acid dependence pathway has been reported on the oxidation of  $\text{S}_2\text{O}_5^{2-}$  by basic fuchsin (Lawal, 1997) and Reduction of triphenylmethane dye by  $\text{S}_2\text{O}_5^{2-}$  (Onu and Iyun, 2001). The result in this differs from Babatunde *et al.*, 2013 where enhancement in the rate was obtained by increase in hydrogen ion in the reduction of methylene blue with  $\text{S}_2\text{O}_5^{2-}$ .

Investigation of the effect of ionic strength on the rate of reaction shows negative salt effect. The slope of the plot of  $\log k_2$  versus  $\sqrt{I}$  was found to be -1.05 (Figure 4.23). This observation is a common feature of reaction occurring between positive and negative species, where the product of the charges is negative at the transition state (Wilkins, 1994).

The product analysis was carried out qualitatively, sulphate ion was identified by quantitative precipitation of  $\text{BaSO}_4$  on addition of dilute HCl and  $\text{BaCl}_2$  solution to the reaction products (Vogel, 1961). To establish whether free radical was important in this reaction, acrylamide was added to the partially reaction mixture, polymerization would have indicated the presence of free radical. The test was however negative, that is, there is no polymerization,

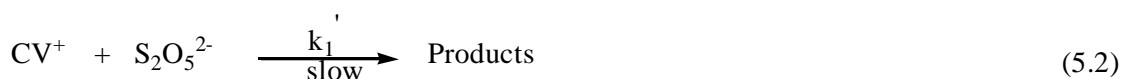
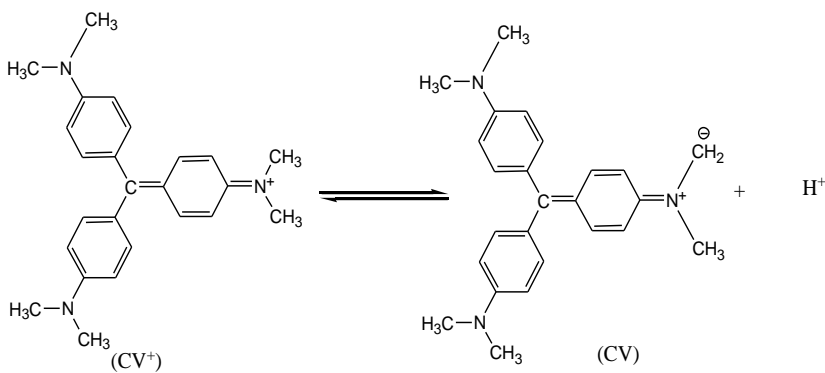
indicating that no noticeable free radicals was present in the reaction mixture. Hence, generation of free radical is not important in this reaction. Similar result was obtained in the reduction of triphenylmethane dye by metabisulphite (Onu and Iyun, 2001).

Addition of varying concentration of  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  decreased the rate of reaction. The observed inhibitive effect of added anions could be explained in terms of columbic forces of attraction, as the activated complex in this reaction is made up of oppositely charged species, bringing in negative charged species would lead to overall repulsion, thereby decreasing the rate of reaction. The ionic strength effect and inhibition by added anion is not surprising, this is due to columbic repulsion which now hindered the reactant partners approaching themselves sufficiently enough for reaction to take place. The inhibitive effect of these ions is quite informative as it suggests that the reactant partners are not joined by any bridging group in the activated complex, a fact in favour of outersphere mechanism (Babatunde, 2009).

Michaelis-Menten plot  $1/k_1$  versus  $1/\text{S}_2\text{O}_5^{2-}$  gave a straight line which passed through the origin (Figure 4.35). This further suggests the absence of the formation of an intermediate complex of significant stability thereby supporting the proposition of the outersphere mechanism for this reaction.

Also, spectroscopic studies indicated no shift from the absorption maxima of 585nm characteristic of crystal violet. This also suggests the probable absence of an intermediate complex of significant stability during the reactions.

Based on the evidence obtained from the kinetic, spectroscopic and other investigations, the following mechanistic steps are proposed for the reaction.



According to equations (5.2) and (5.3), the rate law for the reaction is:

$$\text{Rate} = k_1' [CV^+] [S_2O_5^{2-}] + k_2' [CV] [S_2O_5^{2-}] \quad (5.4)$$

From equation (5.1)

$$[CV] = \frac{K [CV^+]}{[H^+]} \quad (5.5)$$

Substituting equation (5.5) in (5.4), the rate law becomes:

$$\text{Rate} = k_1' [CV^+] [S_2O_5^{2-}] + \frac{K k_2' [CV^+] [S_2O_5^{2-}]}{[H^+]} \quad (5.6)$$

$$= (a + b [H^+]^{-1}) [CV^+] [S_2O_5^{2-}] \quad (5.7)$$

Equation (5.7) agrees with the experimentally observed rate law (equation 4.11)

where  $a = k_1' = 2.27 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $b = K k_2' = 0.86 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$



## 5.2 Crystal violet-bromate ion system

The result of stoichiometry studies showed that two moles of CV<sup>+</sup> oxidized three moles of BrO<sub>3</sub><sup>-</sup> according to equation (4.2). The stoichiometry of 1:5 has been reported by Iyun and Asala, (1994) in the oxidation of methylene blue by bromate ion, whereas, stoichiometry of 5:2 has been reported by Thompson 1971, Iyun 1990 and Lohdip *et al.*, 1996 in the redox reaction of bromate and vanadyl ion, bromate and catechol and bromate and aldehyde respectively.

The linearity of the pseudo-first order plots suggest a first order dependence of reaction rate on [CV<sup>+</sup>] under the experimental condition employed in this investigation. The order of the reaction with respect to [BrO<sub>3</sub><sup>-</sup>] was also found to be one by plotting log k<sub>1</sub> versus log [BrO<sub>3</sub><sup>-</sup>] (Figure 4.13). The reaction is therefore second order overall and the second order rate constant k<sub>2</sub> was determined to be k<sub>2</sub> = (38.47 ± 0.26) dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (Table 4.2). Similar second order dependence have been reported for the reaction of the same oxidant with methylene blue and tetrahedral cobalt(II), Iyun and Asala, (1994) and Ayoko *et al.*, (1991) respectively.

The rate of the reaction increased with increase in acid concentration in the range investigated with slope of 2.03 (Figure 4.13). The plot of k<sub>2</sub> versus [H<sup>+</sup>] was linear with positive intercept (Figure 4.20). This indicated two reaction pathways: an acid independent pathway and a parallel acid dependent way. It shows that parallel reactions of protonated and unprotonated species of BrO<sub>3</sub><sup>-</sup> occurs as in most other reactions of BrO<sub>3</sub><sup>-</sup> and that a protonated equilibrium precedes the electron transfer step (Birk, 1973, Birk and Kozub, 1973, Lohdip and Iyun, 1993). The second order [H<sup>+</sup>] dependence was rationalized in term of the pre-equilibrium, protonation of BrO<sub>3</sub><sup>-</sup> to give H<sub>2</sub>BrO<sub>3</sub><sup>+</sup> (Birk, 1973; Thompson and Knight, 1973; Ayoko *et al.*, 1991; Iyun *et al.*, 1992).



The rate of the reaction was found to increase with increase in ionic strength. Plot of  $\log k_2$  versus  $\sqrt{I}$  gave a slope of 1.04 (Figure 4.24). This positive salt effect suggests that the product of the charges on the reactants in the transition state is +1. This strongly suggests that the principal reactant species in this reaction are most likely  $\text{CV}^+$  and  $\text{H}_2\text{BrO}_3^+$ . This confirms the existence of  $\text{H}_2\text{BrO}_3^+$  as one of the reactive species in the medium (Benson, 1969; Birk, 1978).

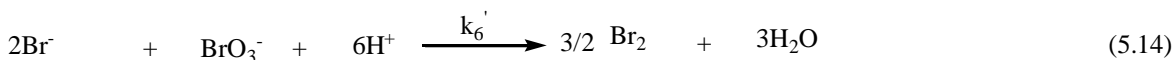
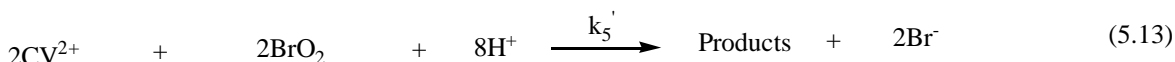
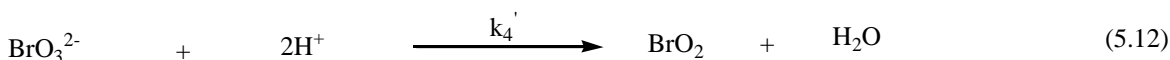
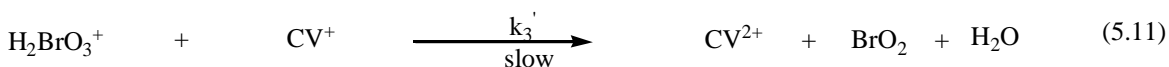
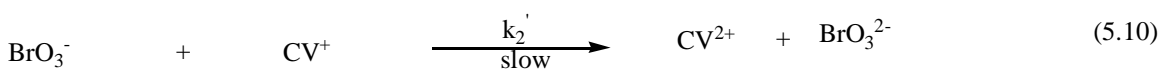
Added anions and cations significantly inhibited the rate of the reaction. Inhibitive effect of added cations could be explained in terms of coulombic forces of attraction, as the activated complex in this reaction is made up of positively charged species, bringing in another positive charged species would lead to overall repulsion, thereby decreasing the rate of reaction. The observed inhibitive effect of added anions could only be explained in terms of ion pairing. The anions might undergo extensive ion pairing with one of the reactant, thereby hindering the chances of the two reactants coming into contact. The inhibitive effects of these ions suggest that outersphere mechanism might be operating (Babatunde, 2009).

The electronic spectra of the reaction mixture were run 2-5 minutes after the initiation of the reaction over the range 500-700 nm. The spectra obtained showed no shift from the  $\lambda_{\text{max}}$  of 585 nm characteristic of crystal violet. The absorbance was also not enhanced. This suggests that there is most likely no complex formation prior to the electron transfer step suggesting that the reaction most probable occur by the outersphere mechanism.

Test for polymerization of acrylamide was performed. The result did not yield positive results, suggesting the probable unimportance of free radicals in this reaction. Michaelis-Menten plot of  $1/k_1$  versus  $1/\text{BrO}_3^-$  (Figure 4.36) was linear with zero intercept, further suggesting the absence of pre-electron transfer complex formation in this reaction thus

supporting the proposed mechanism. This view is reinforced by the observed anion inhibition which is characteristics of the outersphere mechanism. Product analysis was carried out, bromine was confirmed to be present by formation of reddish brown vapour with irritating smell and acidic to litmus paper.

On the basis of the above, the following reaction scheme is proposed for this reaction.



With equations (5.10) and (5.11) as the rate determining step, the equation for the reaction can be written as:

$$\text{Rate} = k_2'[\text{CV}^+][\text{BrO}_3^-] + k_3'[\text{CV}^+][\text{H}_2\text{BrO}_3^+] \quad (5.15)$$

From equation (5.9)

$$[\text{H}_2\text{BrO}_3^+] = K[\text{BrO}_3^-][\text{H}^+]^2 \quad (5.16)$$

Substitution of equation (5.16) into (5.15) leads to:

$$\text{Rate} = (k_2' + k_3'K[\text{H}^+]^2)[\text{CV}^+][\text{BrO}_3^-] \quad (5.17)$$

$$= (c + d[\text{H}^+]^2)[\text{CV}^+][\text{BrO}_3^-] \quad (5.18)$$

Equation (5.18) agrees with the experimentally observed rate law (equation 4.12)

where  $c = k_2' = 9.22 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  and  $d = k_3'K = 1.16 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$

### 5.3 Crystal violet- hypochlorite ion system

Stoichiometric studies show that one mole of the dye is consumed by two moles of the oxidant. Similar stoichiometry has been reported by Muhammed *et al.*, (2011) in the reaction of crystal violet with chlorate ion.

The rate of electron transfer is first order in each  $[CV^+]$  and  $[ClO^-]$ , at constant  $[H^+]$  and the reaction is second order overall. The second order rate constant  $k_2$  was determined to be  $k_2 = (52.53 \pm 0.41) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and is displayed in Table (4.3). Second order kinetics was also observed in the reaction of crystal violet by chlorate ion (Muhammed *et al.*, 2011).

The rate of the reaction was found to increase with increase in  $[H^+]$  with the slope of 1.08 (Figure 4.18). Plot of  $k_2$  versus  $[H^+]$  was linear without an intercept. This indicates that equilibrium between the protonated and deprotonated forms of the reactant prior to the rate determining step is rapid, and that the equilibrium constant for protonation is small and not complete even at high acidities, that is only the protonated form is reactive (Gupta and Gupta, 1984). The increase in rate with increased  $[H^+]$  observed in this study was also observed by Muhammad *et al.*, (2011) in its reaction of crystal violet with chlorate.

The rate of reaction was neither affected by changes in the ionic strength nor the dielectric constant of the reaction medium. These two observations suggest that one of the reacting species in the rate determining step is neutral. The zero salt effect is expected, since in the rate determining step, a charged species and a neutral molecule are reacting. This assertion

is buttressed by the fact that the reaction rate was not affected by changes in the dielectric constant of the reaction medium.

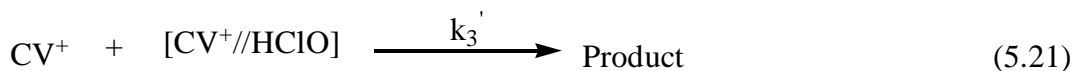
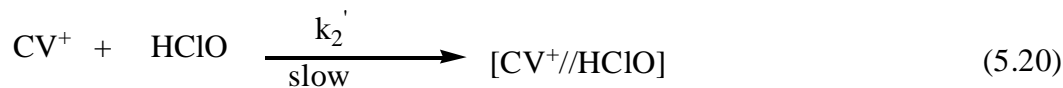
On monitoring the spectra of the reaction mixture 2-3 minutes after initiation of the reaction between the wavelengths 500 – 700 nm, after which a similar run was carried out for the crystal violet alone, there was neither a shift in the wavelength of maximum absorption of the crystal violet ion nor enhanced absorbance, suggesting that there is no innersphere complex formation and confirming the absence of intermediate complex.

A further evidence for probable operation of the outersphere mechanism for this reaction is provided by the catalysis of added ions (Table 4.9) and the Michaelis – Menten plot of  $1/k_1$  versus  $1/[\text{ClO}^-]$  (Figure 4.37) which was linear and passed through the origin.

Addition of acrylamide solution to partially oxidized reaction mixture with addition of excess methanol gave no gel formation, indicative of the likely absence of free radicals in the reaction mixture. The catalysis of added ions on the reaction rate is suggestive of the reaction proceeding through the outersphere mechanism (Adegite *et al.*, 1977).

Qualitative test for chloride ion was carried out. Chloride ion was confirmed by precipitation of  $\text{HNO}_3$  and  $\text{AgNO}_3$  which further dissolve in  $2 \text{ mol dm}^{-3} \text{ NH}_3$  solutions.

Based on the above results, it is evident that the reaction is probably operating through the outersphere mechanism. The following mechanism is hereby proposed for the reaction.



According to equation (5.20), the rate law for the reaction is:

$$\text{Rate} = k_2' [\text{CV}^+] [\text{HClO}] \quad (5.22)$$

From equation (5.19)

$$[\text{HClO}] = K [\text{ClO}^-][\text{H}^+] \quad (5.23)$$

Substitution of equation (5.23) into (5.22) leads to:

$$\text{Rate} = Kk_2' [\text{ClO}^-][\text{CV}^+][\text{H}^+] \quad (5.24)$$

Therefore:

$$\text{Rate} = (g[\text{H}^+]) [\text{CV}^+][\text{ClO}^-] \quad (5.25)$$

Equation (5.24) is related to equation (4.14), and is consistent with the experimentally observed rate law:

$$\text{where } g = Kk_2' = 6.16 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

#### 5.4 Crystal violet-periodate ion system

The stoichiometric studies showed that one mole of crystal violet was consumed by two moles of periodate ion. Similar stoichiometry has been reported for the reduction of tetraoxiodate(VII) by n-(2-hydroxyl)ethylenediamminetriacetocobalt(II) ion and azide in acidic medium respectively (Vivekanandam and Ramachandran, 1982 , El-Idris 1991 and Onu *et al.*, 2009,).

The rate of the reaction of  $\text{IO}_4^-$  with crystal violet is first order in [crystal violet], while the rate is zero order in  $[\text{IO}_4^-]$ , thus the  $k_1$  evaluated from the slopes of the pseudo-first order plots were constant irrespective of the concentration of the periodate ions. Thus, over the range  $2 \times 10^{-3} \leq [\text{IO}_4^-] \leq 12 \times 10^{-2} \text{ mol dm}^{-3}$  at  $[\text{H}^+] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,

$I = 0.50 \text{ mol dm}^{-3}$  (NaCl) the first order rate constant  $k_1$  was determined to be  $k_1 = (6.89 \pm 0.032) \times 10^{-2} \text{ s}^{-1}$ .

The rate of the redox process can be represented as:

$$\frac{-d[\text{CV}^+]}{dt} = k_1[\text{CV}^+] \quad (5.26)$$

The zero-order dependence observed in this study is not common in reaction of periodate ions. Lawal (1997) reported zero order dependence of rate on  $[\text{IO}_4^-]$  in its reaction of periodate with triphenylmethane dye. First order dependence of rate on each of the reactants is the most commonly encountered in the reaction of periodate ion (Kassim and Sulfab, 1991; Lohdip, 1989, Edokpayi, 2011).

The reaction rate was found to increase with increase in  $[\text{H}^+]$ , plot of  $\log k_1$  versus  $\log [\text{H}^+]$  shows an order of 0.97 (Figure 4.17). Plot of  $k_1$  versus  $[\text{H}^+]$  was linear with positive intercept. This kind of acid dependence shows that there is rapid pre-equilibrium between the protonated and deprotonated forms, and the value of the protonation equilibrium constant is great enough that at higher acidity, protonation is almost complete, leading to a limiting rate, i.e both the protonated and unprotonated forms are reactive (Gupta and Gupta, 1984). Similar acid dependence pathways have been reported for reactions of periodate (El-Idris, 1991; Lohdip, 1989; Birk and Kozub, 1978; Edokpayi, 2011).

The fact that both the protonated and unprotonated path was observed in this study implies that both  $\text{IO}_4^-$  and  $\text{H}_4\text{IO}_6^-$  are participating and that  $\text{H}_4\text{IO}_6^-$  is the dominant reactive species in acid for this redox reaction (Lawal, 1997).

The redox reaction showed positive salt effect, that is, the rate of reaction increased with increase in ionic strength from 0.2-1.0 mol  $\text{dm}^{-3}$  (NaCl). The plot of  $\log k_1$  versus  $\sqrt{I}$  gave a straight line with a slope of 1.13, suggesting that the product of the charges on the activated complex is positive (Benson, 1969; Birk, 1978).

The test for free radical was negative suggesting that free radical is not involved in the reaction. Similar observation was made in the reaction of periodate with triphenylmethane dye (Lawal 1997). In addition to the establishment of the absence of free radical in this reaction, iodate ions were also identified qualitatively as reaction product.

Also, by reacting equimolar amount of the dye and periodate at  $[\text{H}^+] = 5.00 \times 10^{-2}$  mol  $\text{dm}^{-3}$  and  $I = 0.50$  mol  $\text{dm}^{-3}$  (NaCl) after the completion of the reaction, a colourless solution was obtained and the UV spectra of the product showed no absorption peak at  $\lambda_{\text{max}}$  585 nm. This indicates the destruction of the quinoid structure that gives the dye colour.

Added anions and cations were observed not to catalyze the reaction. The non catalysis by these ions suggests that the reaction occur by the innersphere mechanism. Non catalysis of the reaction rate by added ions has been reported as characteristic of innersphere pathway. (Adegite *et al.*, 1997 and Shallangwa *et al.*, 2004). There is shift in the  $\lambda_{\text{max}}$  from 585-620 nm, when reactants were mixed together and the electronic spectra were recorded after two minutes of mixing. This suggests the presence of intermediate complex formation.



On the basis of the spectroscopic evidence for an intermediate complex and the rationalization of  $\text{IO}_4^-$  reactions, the innersphere mechanism is probably operating. Most redox reactions of  $\text{IO}_4^-$  are of the innersphere type due to the fact that the oxygen in  $\text{IO}_4^-$  acts as bridging atoms (El-Eziri and Sulfab, 1977). Therefore, majority of the oxidation reactions of periodate seems to proceed via the innersphere mechanism (Kassim and Sulfab, 1981; Sulfab and Abdelkhalek, 1981; Vivekanandam and Ramachandran, 1983; and Bugaje, 2006) and therefore proposed for this reaction.



From equation 5.29, (5.30)

$$\text{Rate} = k_3' [\text{CVHIO}_4^+]$$

Substitution from equation 5.28 leads to:

$$\begin{aligned} \text{Rate} &= \frac{k_3' k_2'}{k_{-2}'} [\text{CVH}^{2+}] [\text{IO}_4^-] \\ &= k_3' k_2' [\text{CVH}^{2+}] [\text{IO}_4^-] \end{aligned} \quad (5.31)$$

Applying steady state hypothesis to  $\text{CVH}^{2+}$  leads to:

$$[\text{CVH}^{2+}] = \frac{k_1' [\text{CV}^+] [\text{H}^+]}{k_{-1}' + k_2' [\text{IO}_4^-]} \quad (5.32)$$

Substitution of equation 5.32 into 5.31 gives:

$$\text{Rate} = \frac{k_3 k_2 k_1 [\text{CV}^+][\text{H}^+][\text{IO}_4^-]}{k_{-1} + k_2 [\text{IO}_4^-]} \quad (5.33)$$

If  $k_2 [\text{IO}_4^-] \gg k_{-1}$ , then

$$k_{-1} + k_2 [\text{IO}_4^-] \text{ is approx. } = k_2 [\text{IO}_4^-]$$

then equation 5.33 becomes:

$$\begin{aligned} \text{Rate} &= \frac{k_1 k_3 k_2 [\text{CV}^+][\text{H}^+][\text{IO}_4^-]}{k_2 [\text{IO}_4^-]} \\ &= k_1 k_3 [\text{CV}^+][\text{H}^+] \end{aligned} \quad (5.34)$$

$$\text{or Rate} = k [\text{CV}^+][\text{H}^+]$$

where  $k = e + f$  to conform to the observed rate law in equation (4.13)

$$e = 1.49 \text{ s}^{-1} \text{ and } f = 1.8 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

## CHAPTER SIX

### 6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

#### 6.1 Summary

The kinetics study of the redox reactions of crystal violet with some oxyanions ( $S_2O_5^{2-}$ ,  $BrO_3^-$ ,  $IO_4^-$  and  $ClO^-$ ) in aqueous acid solution was carried out. The stoichiometry of 1:1 was observed for  $CV^+-S_2O_5^{2-}$ , 2:3 for  $CV^+-BrO_3^-$  and 1:2 for  $CV^+-IO_4^-$  and  $CV^+-ClO^-$  systems respectively.

The reactions were second order at constant  $[H^+]$  for all the systems except that of crystal violet with  $IO_4^-$  which was first order. Apart from the crystal violet- $S_2O_5^{2-}$  system which showed inverse first order hydrogen ion dependence pathways, acid dependent pathways was

observed for the crystal violet- $\text{ClO}^-$ , whereas acid dependent and acid independent pathways were observed for crystal violet- $\text{IO}_4^-$  and crystal violet- $\text{BrO}_3^-$  systems respectively.

The reactions are therefore in conformity with the following rate equations:

$$\frac{-d[\text{CV}^+]}{dt} = (a + b [\text{H}^+]^{-1})[\text{CV}^+][\text{S}_2\text{O}_5^{2-}] \quad (6.1)$$

$$\frac{-d[\text{CV}^+]}{dt} = (c + d [\text{H}^+]^2)[\text{CV}^+][\text{BrO}_3^-] \quad (6.2)$$

$$\frac{-d[\text{CV}^+]}{dt} = (e + f [\text{H}^+])[\text{CV}^+] \quad (6.3)$$

$$\frac{-d[\text{CV}^+]}{dt} = (g [\text{H}^+])[\text{CV}^+][\text{ClO}^-] \quad (6.4)$$

where  $a = 2.27 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 0.86 \text{ s}^{-1}$ ,  $c = 9.22 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $d = 1.16 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$ ,

$e = 1.49 \text{ s}^{-1}$ ,  $f = 1.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $g = 6.16 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ .

The second order rate constants for the various systems were observed as follows:

Crystal violet- $\text{S}_2\text{O}_5^{2-}$  reaction, ( $k_2 = 23.57 \pm 0.45 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )

Crystal violet- $\text{BrO}_3^-$  reaction, ( $k_2 = 38.47 \pm 0.26 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )

Crystal violet- $\text{ClO}^-$  reaction, ( $k_2 = 52.53 \pm 0.41 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )

Crystal violet- $\text{IO}_4^-$  reaction, ( $k_1 = (6.89 \pm 0.032) \times 10^{-2} \text{ s}^{-1}$ )

All reactions were sensitive to change in ionic strength except the crystal violet- $\text{ClO}^-$  which shows no dependent on ionic strength. Except in crystal violet- $\text{ClO}^-$  system where added anions increase the rate of reaction and crystal violet- $\text{IO}_4^-$  where anions had no effect on the rate of reaction, added anions inhibited the rate of reactions for the rest of the systems.

Evidence of intermediate complex formation was suggested for the crystal violet- $\text{IO}_4^-$  reactions by the shift in  $\lambda_{\text{max}}$  from 585-620 nm and no shift was observed for the other systems. Free radicals were not observed for all the systems. Thus the results obtained in this study show that crystal violet- $\text{S}_2\text{O}_5^{2-}$ , crystal violet- $\text{BrO}_3^-$  and crystal violet- $\text{ClO}^-$  reactions could be said to be occurring through the outersphere mechanism, while the crystal violet- $\text{IO}_4^-$  reaction occurs via the innersphere mechanism. Therefore such mechanisms were proposed for the reactions respectively.

## 6.2 Conclusion

On the basis of the results of these investigations, absence of and/or presence of kinetic and/or spectroscopic evidence for complex formation prior to electron transfer and non-conformity of the results with Michaelis-Menten plots, rationalization of previous results, outersphere mechanism is postulated for the  $\text{CV}^+$ - $\text{S}_2\text{O}_5^{2-}$ ,  $\text{CV}^+$ - $\text{BrO}_3^-$  and  $\text{CV}^+$ - $\text{ClO}^-$  reactions, whereas, innersphere mechanism is postulated for  $\text{CV}^+$ - $\text{IO}_4^-$  reaction.

## 6.3 Recommendation

It is recommended that:

1. further studies should be carried out on the activated parameters of these reactions,
2. thorough analysis to identify the organic product should be made, and

3. more systems involving other oxidants and reductants should be studied for more information on the chemical characteristics of crystal violet.

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