“Role of Inhibitors in Atmospheric Catalytic Autoxidation of Aqueous Sulfur Dioxide in Acidic Medium”

‘‘अम्लीय माध्यम में जलीय सल्फरडाईऑक्साइड के वातावरणीय उत्प्रेरकीय स्वतः ऑक्सीकरण में संदमको की भूमिका’’

A
Thesis
Submitted to the
University of Kota, Kota
For the Award of Degree of
DOCTOR OF PHILOSOPHY
In the Faculty of Science (Chemistry)

By
ARUN KUMAR SHARMA

Supervisor:	Co-Supervisor:
Dr. D.S.N. PRASAD	**Dr. RASHMI SHARMA**
Lecturer in Chemistry	Lecturer in Chemistry
Department of Chemistry	Department of Chemistry
Govt. P.G. College, Jhalawar, Rajasthan	S.P.C. Govt. College, Ajmer, Rajasthan

2016

Dedicated to
my be loved
Parents
Late. R.P. Sharma
&
Mrs. Vimla Sharma

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled **"Role of Inhibitors in Atmospheric Catalytic Autoxidation of Aqueous Sulfur Dioxide in acidic Medium"** *embodies a record of the results of investigations carried out by* **Mr. Arun Kumar Sharma** *under my guidance. I am satisfied with the analysis of data, interpretation of results and the conclusions drawn.*

He has completed the residential requirements as per rules.

I recommend the submission of thesis.

Date:

Dr. D.S.N. Prasad
SUPERVISOR
Lecturer in Chemistry
Department of Chemistry
Govt. P.G. College, Jhalawar (Raj.)

Dr. Rashmi Sharma
CO-SUPERVISOR
Lecturer in Chemistry
Department of Chemistry
S.P.C. Govt. College, Ajmer (Raj.)

Declaration

I hereby declare that the Research work on "**Role of Inhibitors in Atmospheric Catalytic Autoxidation of Aqueous Sulfur Dioxide in acidic Medium"** has been carried out by me under the Guidance of **Dr. D.S.N. Prasad**, Lecturer, Department of Chemistry, Govt. P.G. College Jhalawar and **Dr. Rashmi Sharma**, Lecturer, Department of Chemistry, S.P.C. Govt. College Ajmer.

This work has been done for partial fulfillment of the requirement for the award of the degree of **"Doctor of Philosophy"** in Chemistry.

Further it is mentioned that research data and results cited in the thesis are original and independent findings of my research work.

Date: ***Arun Kumar Sharma***

Place: Govt. P.G. College Jhalawar

ACKNOWLEDGEMENT

On the completion of a gigantic task which at the onset appeared so difficult, there are a mixed feeling of joy, satisfaction, sense of fulfillment and achievement.

Foremost, I would like to express my sincere gratitude to my supervisor **Dr. D.S.N. Prasad, Lecturer, Department of Chemistry, Govt. P.G. College Jhalawar and Co-Supervisor Dr. Rashmi Sharma, Lecturer, Department of Chemistry, S.P.C. Govt. College Ajmer** for the continuous support during my Ph.D. study and research, for their motivation, enthusiasm and immense knowledge. I highly appreciate their patience and allowing me the liberty to work on my own passion. Above all and the most needed, they provided me unflinching encouragement and patronage in their unique simplicity and cheerful way. Their guidance helped me in all the time of research and writing of this thesis.

I am highly thankful to **Dr. Pradeep Parasher, Lecturer, Department of Chemistry, Govt. P.G. College Jhalawar** for his guidance, generous help, perpetual encouragement and abundant interest throughout the tenure of this research.

I am grateful to **Principal** Govt. P.G. College, Jhalawar and **Mrs. Pratibha Sharma,** Head Department of Chemistry, Govt. P.G. College, Jhalawar for extending me all the research facilities and encouragement time to time. I am also thankful to **Dr. A. K. Gupta, Dr. Jaibeer Singh, Mrs. Jyothi Pathak and Mr. Bajrang Vishvakarma** for their co-operation and valuable assistance.

Especially I would like to give my special thanks to my Seniors **Dr. Faiyaz Hussain and Dr. Sameena Begum** for their co-operation, moral support, generosity and encouragement during my research work.

It is difficult to express my deep sense of feeling to **Mrs. Ratna Prasad D.L. Harshita, and D.V. R. Harshvardhan** for their best suggestions.

I would like to thank **Dr. P. Bhagchandani, Dr. L.C. Heda, Dr. Shveta Acharya, Dr. Vijay Chauhan, Dr. Swati Sharma** for extending all possible Co-operation.

I would also like to express my deep sense of gratitude to the affection and support shown to me by my father **Late R.P. Sharma and my mother Vimla Sharma.** I take this opportunity to dedicate this work to my parents who have made me what I am, my brothers **(Deepak, Hament, Rahul and Sisters (Deepika and Versha), my Bhabhi (Tony)** who gave me consistent support throughout my research. I learnt to aspire to a career in research from my parents in my childhood and later from my life partner **Rakhi Sharma**.

No research is possible without the library, the centre of learning resources. I take an opportunity to express my gratitude to all the library staff for their services.

I wish to express my gratitude towards all the lab assistants, store keepers for their extended cooperation during my practical work. I am also indebted and grateful to my friends and colleagues who shared their experiences and helped me in difficulties. Thank you all for the encouragement and support for helping me in completion of my work.

Above all I owe it all to the almighty god for granting me the wisdom, health and strength to undertake this research work and enabling me to its completion. All of you made it possible for me to reach this last stage of my endeavor thank you from my heart-of-hearts.

I am unable to express in words my sincere thanks to **Mr. Sushil Jangid** (Sun Computers, Beawar) whose contribution in producing this work in limited time are uncountable.

Place : Jhalawar

Dated: **February, 2016** **Arun Kumar Sharma**

CONTENTS

CHAPTER - I

INTRODUCATION

This Chapter Briefly Reviews the Chemistry of S(IV) and Important Autoxidation Mechanism

1. AIR POLLUTION

The study of air pollution has only been of major interest to the scientific community since the end of World War II. The earliest perceived problems were those related to the incomplete combustion of coal, soot and ash abounded in the major industrial cities of the world. Air pollutants are divided into two general categories:(Dentener et al 1994)[1]

1) Primary : Those emitted directly into the atmosphere, and

2) Secondary : Those formed by subsequent reactions of primary pollutants. The first category includes soot, carbon dioxide, carbon monoxide, sulphur oxides, nitrogen oxides and hydrocarbons. The latter includes sulphuric and nitric acids, ozone and oxygenated organic compounds. It is the intent of this research to study how two primary pollutants, soot and sulphur dioxide, interact to form sulphuric acid.

2. ACID RAIN PRECURSORS

A large number of organic and inorganic chemical species are released into the atmosphere by anthropogenic and natural sources. The subsequent photochemical and thermal reactions of these species in gas and aqueous phase form the backbone of the atmospheric chemistry. The atmospheric reactions of SO_2 and NO_x etc. are major acid rain precursors and are responsible for acidification of various forms of atmospheric water. Studies in India and abroad have shown that anthropogenic sources in the atmosphere are the major contributors of SO_2 and NO_x which are transformed in to acids such as HNO_2, HNO_3, H_2SO_3 and H_2SO_4. Several reports on acid rain have shown the contribution of nitric acid and sulphuric acid to decrease the pH of rain water. (Acker et al 2001[2] 2005[3]; Brimblecombe1996[4]).

A large number of laboratory and field studies on acid rain chemistry have been carried out globally[5,6]. Turning to our own country, field studies on rain water acidity have been carried out by several workers notably, kulshreshtha et al (1995,1996,2003)[7,8,9], Banerjee et al (2008)[10], Saxena et al (1991)[11], khemani et al (1989,1994)[12-13] and Gupta et al(2000)[14]

3. TYPES OF ACID PRECIPITATION

There are two types of acid precipitation

3.1 Wet Depositions

These include various forms of atmospheric water such as rain, fog, mist, dew and snow. Rain water in atmosphere is buffered by the dissolution of atmospheric CO_2.

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3 \qquad (1)$$

The calculation using equation (1) predicts that in an unpolluted and dust free atmosphere, the background pH of rain water should be 5.5 – 7.5 However natural pH of a region may be quite different than this value due to the presence of suspended particulate matter (SPM). If the SPM loaded heavily by alkaline material, as in Rajasthan (India) the pH of the rain water will be high and often exceed 8.0 on the other hand, if the soil is acidic in nature, the rain water pH shall be low. It is rightly indicated that the trace constituents, depending upon the location can significantly change this pH value. Other sulphur compounds like H_2S and CH_3SCH_3 also contribute to acid rain by their prior oxidation in to SO_2[15] NO_x is formed by biomass burning, lightening, soils, and high temperature fuel combustion.[16]

3.2 Dry Acid Precipitation

It refers to the deposition of acidic gases such as NO_x SO_2 etc and particles like nitrate, sulphate, chloride etc. in dry atmosphere.

4. ATMOSPHERIC SULPHUR- SOURCES AND HEALTH ASPECTS

Sulphur as a pollutant exists mainly in three forms, reduced as hydrogen sulphide (H_2S) and oxidized as sulphur dioxide (SO_2) and sulphur trioxide (SO_3) The two oxidized forms, which are species of the oxidation states S(IV) and S(VI), also exist as ionic species; bisulphite (HSO_3^{-1}), sulphite (SO_3^{-2}), bisulphate (HSO_4^{-1}) and sulphate (SO_4^{-2}). These sulphur containing species have many sources. They can come from man's burning of fossil fuels as well as from the decomposition and combustion of organic materials, sea salts and volcanoes. Man has little, if any, control over these natural sources of pollutant sulphur, which can contribute as much as 50 percent of the globally emitted sulphur each year[1]. It is the remaining 50 percent which is of major interest in the development of air pollution control strategies. The sulphur dioxides contribute to the formation of acid rain and directly to deleterious health effects. Respiratory and cardiopulmonary problems have been shown to be caused by sulphur dioxide[2], as well as asthmatic attacks and eye irritations. The concentrations needed to cause serious health effects, however, are rarely achieved though. The formation of acid rain is a source of major interest and concern these days. Acid rain is caused by nitric and sulphuric acids which are formed by the oxidation of nitrogen oxides (NO_x) and sulphur dioxide. The increased acidity of the precipitation (down to pH about 3.0 has had many deleterious effects. Many lakes have become too acidic to sustain aquatic life, most fish not being able to live with a pH below 4.5[3]. The acidity also affects the plant life, both by attacking the leaves and branches of the vegetation and by leaching many of the nutrients in the soil into the run off.

Its effects on buildings and statues as many older structures, especially those constructed of sandstone or marble, are literally dissolving. Knowledge of a problem is existence is not always the same as understanding its cause or how to prevent it. Simplistically, sulphuric acid is formed by the oxidation and dissolution of SO_2 But the concentration of sulphate present in the atmosphere is much greater than that which can be accounted for by the preceding reaction[1]. Clearly, additional mechanisms for the oxidation of SO_2 must play an important role in the atmosphere.

$$SO_2 + H_2O + 0.5O_2 \longrightarrow H_2SO_4 \qquad (2)$$

5. SO_2 OXIDATION PATHWAYS

The atmospheric oxidation of acid precursors in both gas and aqueous phases occurs though the following pathways.

5.1 Gas Phase Oxidation

The oxidation of SO_2 is brought about by hydroxyl and other radicals and compounds formed by photochemical reaction. The chemistry of formation of OH radicals is as follows

$$NO_2 + h\upsilon\ (\lambda < 430\ \text{nm}) \longrightarrow O\,(^3P) + NO \qquad (3)$$

$$O\,(^3P) + O_2\,(^+M) \longrightarrow O_3\,(^+M) \qquad (4)$$

$$O_3 + NO \longrightarrow O_2 + NO_2 \qquad (5)$$

$$O_3 + h\upsilon\ (\lambda < 290\text{ -}306\ \text{nm}) \longrightarrow O\,(^1D) + O_2 \qquad (6)$$

$$O\,(^1D) + H_2O \longrightarrow 2OH \qquad (7)$$

The atmospheric concentrations of OH radicals is estimated to be (6 $\underline{+}$3) x 10^6 molecule/cm^{-3} (Brandt and van Eldik 1995[17] calvert and stockwell 1984[18]).

The reaction of OH radical with SO_2 is believed to proceed as follows

$$SO_2 + OH\,(^+M) \longrightarrow HOSO_2\,(^+M) \qquad (8)$$

$$HSO_2 + O_2 \longrightarrow SO_3 + HO_2 \qquad (9)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \qquad (10)$$

The overall reaction can, therefore be written as follows:

$$OH + SO_2\,(^+M+O_2+H_2O) \longrightarrow H_2SO_4 + HO_2\,(^+M) \qquad (11)$$

5.2 Aqueous Phase Oxidation of S (IV) by H_2O_2 and O_3

In atmosphere, hydrogen peroxide is formed as a result of photochemical free radical reactions

$$HO + CO \longrightarrow H + CO_2 \quad (12)$$

$$H + O_2 (^{+}M) \longrightarrow HO_2 (^{+}M) \quad (13)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad (14)$$

$$HO_2 + H_2O \longrightarrow H_2O.HO_2 \quad (15)$$

$$H_2O.HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 + H_2O \quad (16)$$

Due to very high value of Henary constant (7 x 10^4 mol L^{-1} atm^{-1} @ 25 °C) the concentrations of H_2O_2 in aqueous phase is relatively high. The oxidation of S (IV) is catalysed by hydrogen ions and hence with the increase in the pH, the rate decreases. The following gross mechanism has been proposed (Hoffmanand Edwards 1975[19] Halperin and Taube 1952[20]).

$$HSO_3^{-} + H_2O_2 \longrightarrow {}^{-}O_2SOOH + H_2O \quad (17)$$

$${}^{-}O_2SOOH + HA \longrightarrow H_2SO_4 + A^{-} \quad (18)$$

Where HA is H^+ or other acid.

In troposphere ozone is usually found in 30-60 ppb range and formed as results of photolytic results of NO_2. Its solubity in water is much lower than that of H_2O_2 due to the low value of Henary Constant ($1x10^{-2}$ mol L^{-1} atm^{-1}). A simplified mechanism for the reaction is as follows. (Halperin and taube 1952[20] , Penkett et al 1979[21], Penkett 1972[22], Larson et al 1978[23], Martin 1984[24] etc)

$$O_3 + HSO_3^{-1} + H_2O \longrightarrow \text{INTERMEDIATE} \longrightarrow SO_4^{-2} + H^+ + O_2 \quad (19)$$

The rate of reaction increases, when pH is increased.

5.3 Aqueous Phase Speciation of SO_2

The atmospheric oxidation of SO_2 by O_2 in aqueous media has been the subject of numerous studies, and the subject matter of several reviews, monographs and papers, notably by Kuo et al (2006)[28], Clemitshaw (2006)[109], Brandt and Van eldik, (1995)[17], Calvert and Stockwell, (1984)[18], Gupta (2002)[111], Huie and Peterson, (1983)[72], Hoffmann and Boyce (1983)[26], Hoffmann and Jacob (1984)[25], Hermann, (2000)[87], Manoj et al (2000)[56], Rani et al (1992)[95], Manoj et al (1999)[58], Prasad et al (1991)[51], Martin (1984)[24], Kraft and van Eldik (1989)[27] etc.

$$S(IV) + 0.5O_2 \longrightarrow S(VI) \qquad (20)$$

The oxidation of SO_2 (aq.) by O_2 is slow but is strongly catalyzed by homogenous and heterogeneous catalysts (Prasad et al., 1991[53], 1992[50], 1994[66], 2003[59], Rani et al., 1991[55], 1992[50], Bhargava et al., 1992[57], 1993[52], Gupta et al., 1999[45], 2000[37], 2001[46], 2002[111], 2004[47], Manoj et al., 1999[45], 2000[37], Martin 1984[24], Hoffmann and Jacob, 1984[25], Hoffmann and Boyce, 1983[26], Kraft and van Eldik, 1989[27], Brandt and van Eldik, 1995[17], Kuo et al., 2006).[28] The uncatalysed aqueous SO_2 oxidation is believed to be catalysed by trace metal ions and has been shown to be seized by addition of EDTA. This has been adduced as an evidence for the involvement of trace metal ions viz. iron (III) and Mn (II). EDTA renders these inactive by forming a strong complex.

Although the SO_2 oxidation by O_2 has been the subject of many studies, the mechanism of the reaction is far for settled. Both non radical and radical mechanism have been proposed. It is interesting to point out that reaction is strongly inhibited by alcohol, benzene, and other compounds., pointing to the participation of radical intermediates (Huss et al, 1978[69], 1982a[34], 1982b[70], 1982c[71], Kuo et al, 2006[28], Huie and Peterson, 1983[72], Huie and Neta, 1984[73]) In aqueous solution SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_5^{-2}$, governed by the following equations:

$$SO_{2(g)} + H_2O \overset{K_h}{\rightleftharpoons} SO_2.H_2O_{(aq)} \qquad (21)$$

$$SO_2.H_2O_{(aq)} \overset{K_1}{\rightleftharpoons} HSO_3^{-1} + H^+ \qquad (22)$$

$$HSO_3^{-1} \overset{K_2}{\rightleftharpoons} SO_3^{-2} + H^+ \qquad (23)$$

$$2HSO_3^{-1} \overset{K_3}{\rightleftharpoons} S_2O_5^{-2} + H_2O \qquad (24)$$

K_h is Henry's constant and K_1, K_2 are acid dissociation constant. K_3 is the format ion constant for $S_2O_5^{-2}$ at 25^0 C the values are $K_h = 1.23$ mol L^{-1} atm^{-1}, $K_1 = 1.4 \times 10^{-2}$, $K_2 = 6.24 \times 10^{-8}$, and K_3 is 7.6×10^{-2} The total concentration of dissolved sulphur dioxide [S(IV)] is governed by equilibria (21-24) and is given by equation (25)

$$[S\,(IV)] = (1+k_1\,[H^+]^{-1} + k_1k_2\,[H^+]^{-2})\,[SO_2.H_2O] \qquad (25)$$

The equation shows that the solubility of SO_2 in water increases with increase in pH and it is clear that nature of species of S(IV) depends on pH. For example in pH range 4.0 – 5.6 major species is HSO_3^{-1} and above pH 7.0 SO_3^{-2} is dominant species.

6. KINETICS OF HOMOGENOUS METAL ION CATALYSED AUTOXIDATION REACTIONS

In the atmosphere, the anthropogenic sources and soils are the major contributor of trace metal iron ion (II) / (III), copper ((II), cobalt(II), and nickel (II). The most important metal ions from atmospheric view are iron and manganese (Penkett et al 1979[21], Grgic et al 1991[29], Martin 1984[24] and to extent some copper).

The major studies on iron (III), manganese (II), copper (II), and cobalt (II) catalysed autoxidation of SO_2 in aqueous solution are collected below-

Fe (III) Catalysis – Manoj et al 2008[30], Martin 1984[24], Fuzzi, 1978[31], Brimblecombe and speeding 1974[32] and Hoffmann 1988[33] Huss et al 1982[34]

Mn (II) Catalysis – Wilkosz and Mainka 2008[35] Grigic et al 2007[36] Manoj et al 2000[37] Connick and Zhang 1996[38] Berglund et al 1993[39] podkrajsek et al 2004 Huss et1982[34]

Cu (II) Catalysis - Lunak et al 1978[41] Fuller and Crist 1941[42] Grigic et al 1991[29]

Co(II) Catalysis - Hobson et al 1986[43] Srivastava et al 1968[44]

Ag (I) Catalysis - Gupta et al 1999[45] 2001[46]

Os (VIII) Catalysis - Gupta et al 2004[47]

Ni (II) catalysis - Linn Jr et al 1990[48]

Se Catalysis - Bronikowaski et al 2000[49]

7. KINETICS OF HETEROGENOUS PARTICLE SURFACE CATALYSED AUTOXIDATION REACTIONS

The surface area of particles also plays a prominent role in the autoxidation of S(IV). The catalytical particulate materials, which are atmospheric importance include suspended particulate materials free fall atmospheric dust [50], SiO_2 [51], MgO[52], CdO[53], CuO[51], CoO[54-55], MnO_2[56], Ni_2O_3[54,57], Cu_2O[58], Co_2O_3[54-59], CdS[37] , flyash[60-62], Carbonaceous particles[63], minerals and rocks[64-66]

7.1 CATALYSIS BY SUSPENED PARTICULATE MATTER (SPM)– FREE FALL ATMOSPHERIC DUST

Dust is a heterogeneous mixture of several compounds. Its role in catalysing the autoxidation of aqueous sulphur di oxide was studied by Rani et al[50]. The kinetics results were in agreement with rate law.

$$R_{obs} = k_6[S(IV)\ [H^+]^{-1.3} + k_7[dust]^{0.42}\ [S(IV)]^2\ [H^+]^{-1.36} \qquad (26)$$

At pH 5.06 (Acetate buffer) the reaction was slow in the beginning for about 2.5 min and there after it attained the maximum rate. The initial slow reaction was due to surficial catalysis, which is subsequently overtaken by leached metal ion catalysis. EDTA reduces the rate of suspension catalysed reaction by about 80% by arresting the leach ate reaction due to the complexing the metal ions. An increase in the particle size did not affect the rate but led to an increase in the induction period which probably the time taken by metal ions to leach in the solution.

7.2 CATALYSIS BY NON–TRANSITION METAL OXIDE AND OTHER COMPOUNDS

The important features of catalytic autoxidation of non -transition metal oxide such as CdO[53], MgO[52], Silica[51] and some other materials like rocks and minerals [64], glass[53] and flyash[60-62], in their aqueous suspensions are as follows:

1. CdO, MgO and limestone are very efficient catalyst and there appears to be a linear relationship between rate of autoxidation and pH. Obviously, higher is the surface pH, greater is the catalytic activity of oxide.
2. In most of the cases a kinetic order of more than one in S (IV) has been found.

7.3 CATALYSIS BY CARBONACEOUS PARTICLES

Activated carbon and combustion produced soot particles have been studied for their catalytic effect on the oxidation of aqueous S(IV) species by brodzinsky et al 1980[63]. These particles are found to be effective catalysts for the reaction. Combustion produced soots were tested for their catalytic behavior and found to be similar to the activated carbons. The reaction rate was found to be linearly dependent on the concentration of carbon particles in the solution. The rate was found to follow a Langmuir adsorption isotherm for its dependence on oxygen and the product of two adsorption isotherms for

S(IV). The reaction is independent of the pH of the solution when the pH is below 7.6 The reaction does not occur when the pH is above 7.6 The three aqueous S(IV) species are catalyzed in their oxidation by the carbon particles in a similar manner. The pH cut-off is suggested as being a function of the catalytically active sites on the carbon surface. Activation energies for the reactions on the different carbons are all about 8.5 kcal/mole. A possible four-step reaction mechanism is proposed. It consists of the adsorption of a dissolved oxygen molecule onto the carbon surface, followed by the adsorption of two S(IV) molecules or ions. These are oxidized on the surface to sulphate, which desorbs from the surface, regenerating the catalytically active site. Saxena (1993)[65] studied the autoxidation of S(IV) in the acetate suspension of exhaust carbon particles (Automobile dust) The following rate law was given by eq. (27)

$$R_{obs} = k_4[\text{dust}]^{0.5} [S(IV) [H^+]^{-0.8} \qquad (27)$$

The addition of buffer enhance the rate of reaction by leaching the metal ion in to aqueous phase and these metal ions act as a catalyst.

7.4 CATALYSIS BY CdS

Manoj et al (2000)[35] studied the kinetics of autoxidation of S(IV) catalysed by CdS which obeys the rate law (28)

$$-d[S(IV)]/dt = k_3[S(IV)]^2 [H^+]^{-2} + k_4[CdS] [S(IV)]^2 [H^+]^{-1} \qquad (28)$$

Where k_3= 1.17x10^{-12} mol L^{-1}s^{-1}and k_4=4.5x10^{-7} L^{2}mol^{-2}g^{-1}s^{-1} at 30 ^{o}C in acetate buffered medium. The addition of EDTA [(1-3)x10^{-4} mol L^{-1}] reduced the rate only slightly as has been noted by Connick et al [38] The addition of ethanol of oxysulphur radicals[38,67] pointing to the operation of free radical mechanism.

7.5 CATALYSIS BY TRANSITION METAL OXIDES

The transition metals are an integral part of suspended particulate matter (SPM) Since the combustion process release the metals in the atmosphere in the form of their oxides, which are known to be heterogeneous catalysts for several liquid phase reaction of CoO[54-55], Co_2O_3[54,59] , Ni_2O_3[54,57], CuO[51] and MnO_2[56] as catalyst. In each case, the autoxidation led to the formation of sulphate ion as in (29)

$$HSO_3^- + 0.5\,O_2 \longrightarrow SO_4^{-2} + H^+ \qquad (29)$$

The possibity of the catalytic activity of metal oxide suspensions being due to leached metal ions was ruled out by the fact that rates of autoxidation in leachate and blank reaction were found to be almost the same in case of the catalysis by CuO, which dissolves significantly to produce Cu(II) ions, it was shown that the homogenous catalysis due to leached Cu(II) ions was insignificant. This conclusion was reinforced by the fact that addition of EDTA did not have significant effect on reaction rates.

In acetate buffered suspensions, the following kinetics rate law was obeyed.

$$-d[S(IV)]/dt = R_{obs}.= (k_1+k_2[H^+]^{-1})\,[Catalyst]\,[S(IV)] \qquad (30)$$

The proposed mechanism suggest the formation of surficial complex between metal oxide, S(IV) and dioxygen [63,51-55]

A comparison of the rate constant shows the reactivity order $MnO_2>CuO>Co_2O_3>CoO>Ni_2O_3$. Incidently all these oxides, except MnO_2 fails to oxidize S(IV) directly in the absence of oxygen. In the case of MnO_2 which shows the highest catalytic activity, a slow but perceptile oxidation of S(IV) does occur.

In case of CoO and NiO_3 catalysed reaction in acetate buffered acidic medium, the O_2 dependence of the reaction rate was also studied. This way in agreement with the rate law (31)

$$-d[S(IV)]/dt = (k_3+k_4/[H^+])\,[M_xO_y]\,[S(IV)\,][O_2] \qquad (31)$$

The values of k_1 and k_2 for different catalysts are given in Table 1

Table :1.1

Values of k_1 and k_2 for different Catalytic Autoxidation of S(IV)

Catalyst	Temp. ^{o}C	10^4 k_1 L $g^{-1}s^{-1}$	10^9 k_2 mol $g^{-1}s^{-1}$	Ref.
CoO	30	2.7	2.8	27
Co_2O_3	30	11.3	16.4	31
CuO	30	16.6	37	24
Ni_2O_3	30	0.95	3.87	29
MnO_2	30	155	286	28

A study of the kinetics in un buffered suspensions of CoO, CuO, Co_2O_3, and NiO_3 showed the reaction profiles to be biphasic in certain pH ranges, the first stage of the reaction being fast and the second being slower step, the general rate law (32) was observed.

$$R_{obs} = \quad k_0 [S(IV)] + k_2 [M_xY_x] [S(IV)] \qquad (32)$$

The extensive studies with transition metal oxides suggest that the particle surface to be major cause of catalysis, which is in agreement with previous indication of Berresheim and Jaeschke[68] and recent suggestion of Prasad et al[55] that the wetted particles may absorb SO_2 and aid in its subsequent oxidation.

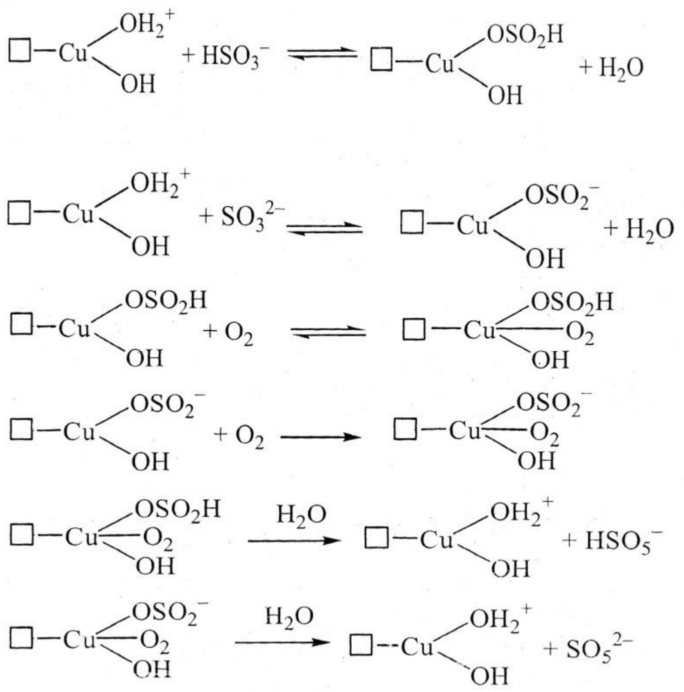
A study of effect of ethanol revealed the surface-catalysed reactions to fall in two categories. Firs categories included the reactions catalysed by MgO, CdO, SiO_2 etc. which were completely inhibited by addition of 0.17 mol L^{-1} ethanol and no reaction was observed for a period of one hour. The second category comprised the reactions catalysed by CdS, Cu_2O, MnO_2, CoO, Ni_2O_3 and CuO in which only a slight retardation in rate was observed.

8. SO_2 OXIDATION MECHANISMS

The proposed mechanisms for the oxidation of SO_2 in the atmosphere can be divided into two general categories; gas phase reactions and heterogeneous aqueous mechanisms. The aqueous mechanisms have traditionally been divided into catalyzed and uncatalyzed reactions. The uncatalyzed reactions can be the reaction of aquated SO_2 and dissolved O_2 in either the presence or absence of ammonia[4-8]. The catalyzed reactions have usually been regarded as those involving the ionic species of transition metals, in particular $Fe^{3+}$and Mn^{2+} [5-13]. Aqueous ozone can also oxidize the SO_2[14]. The gas phase reactions can be divided into homogeneous reactions, photochemical reactions (including free radical mechanisms) and gas surface reactions.

8.1 Non Radical Mechanism

A Non Radical Mechanism generally operates in the catalysis by transition metal oxide and by iron (III) when pH is low. As an example of non- radical mechanism of CuO –catalysed reaction is given below.



(33)

(34)

(35)

(36)

(37)

(38)

$$SO_5^{2-} + H^+ \longrightarrow HSO_5^- \text{ (rapid)} \qquad (39)$$

$$HSO_5^- + S(IV) \longrightarrow 2S(VI) \text{ (rapid)} \qquad (40)$$

The reactivity order for the different transition metal oxide has been found to be $MnO_2 > CuO > Co_2O_3 > CoO > Ni_2O_3$. In the autoxidation mechanism, the adsorbed S (IV) transfer its electrons to matrix M (where M = Cu, Mn, Ni, Co) and S (IV) so formed interact with adjacently adsorbed O_2 , takes back an electron from matrix M and leave off as SO_5^{-2}

8.2 Radical Mechanism

When the sulphur S (IV) autoxidation is inhibited by alcohol and other inhibitors, the reaction operates through oxysulphur radical intermediates (Huss et al 1978[69] 1982[34], 1982[71] 1982[70] Kuo et al 2006[28] Huie and Peterson 1983[72], Huei and Neta 1984[73] was first to propose a free radical mechanism.)

In aqueous solutions even in the absence of any added metal ions, the autoxidation is believed to be catalysed by trace metal ions M^{n+} present as impurities. The transition metal ions which are always present in atmospheric water in trace concentrations undergo one electron change and in general the catalysis proceeds though radical mechanism. The radical mechanism initial proposed by Backstrom has been modified subsequently by inclusion of sulphate ion radical SO_4^{-2} (Hayon 1972)[75] as presented below :

Initiation

$$M^{n+} + SO_3^{2-} \longrightarrow M^{(n-1)+} + SO_3^{-\bullet} \tag{41}$$

$$SO_3^{-\bullet} + O_2 \longrightarrow SO_5^{-\bullet} \tag{42}$$

Propagation

$$SO_5^{-\bullet} + SO_3^{2-} \longrightarrow HSO_5^{-} + SO_3^{-\bullet} \tag{43}$$

$$SO_5^{-\bullet} + SO_3^{2-} \longrightarrow SO_4^{-\bullet} + SO_4^{2-} \tag{44}$$

$$SO_4^{-\bullet} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^{-\bullet} \tag{45}$$

Oxidation

$$HSO_5^{-} + SO_3^{2-} \longrightarrow 2SO_4^{2-} + H^{+} \tag{46}$$

Termination

$$2SO_3^{-\bullet} \longrightarrow S_2O_6^{2-} \quad (47)$$

$$SO_3^{-\bullet} + SO_5^{-\bullet} \longrightarrow S_2O_6^{2-} + O_2 \quad (48)$$

$$SO_5^{-\bullet} + SO_5^{-\bullet} \longrightarrow S_2O_8^{2-} + O_2 \quad (49)$$

Inhibitory effect was explained through scavenging of radicals as in equations (50-51).

$$RCH_2OH + SO_5^{-\bullet} \longrightarrow RCHO + SO_4^{-\bullet} + H_2O \quad (50)$$

$$SO_5^{-\bullet} + RCH_2OH \longrightarrow RCHO + SO_4^{2-} + H_2O \quad (51)$$

Various other rate expressions having different values of the kinetic orders in the reactants can be obtained if a different termination steps is assumed.

$$-d\,[SO_3^{-2}]/dt \;=\; k\,[M^{n+}]^a\,[SO_3^{-2}]^b\,[O_2]^c \quad (52)$$

The values of coefficients a, b, c depends on the choice of termination steps. Most of the studies support the experimental laws (52) (Martin, 1984[24] Gupta et al. 2000[76]).

9 ROLE OF INHIBITORS

Bigelow (1898)[89] was the first to observe the inhibiting effect of alcohols such as methanol, ethanol, propanol, butanol on the rate of the reaction between sodium sulfite and oxygen. The inhibiting effect of alcohols was investigated subsequently by Alyea and Backstrom (1929)[90] The other inhibitors studied are phenols (Altiwicker, 1980)[77], alcohols (J. Ziajka 2003)[91] organic acids (Lee and Rochelle, 1987[78], Grgic et al., 1998[79] , 2007[36] podkrajsek et al 2006[80] wilkosz al 2008[35] Wolf et al., 2000[92]), benzene (Ziajka et al., 1994)[81], toluene, naphthalene, paraffin oil (Pasuik Bronikowska et al., 1997)[82], alpha-pinene, cis – verbenol (Ziajka and Pasuik – Brobikowska, 1999)[83], sobrerol (Pasuik – Bronikowska et al., 1998[84], 1999[93]), myrtenol (Pasuik – Bronikowska, et al., 2000)[85] and others

(Rudzinski and Pasiuk – Bronikowska, 2001[86] 2003[94]). The effect of ammonia has been studied on catalysed S (IV) autoxidation (Manoj et al 1999[95], Mudgal et al 2007[96]).

Hayon et al (1972)[75] proposed a radical mechanism involving $SO_3^{-\bullet}$, $SO_4^{-\bullet}$, $SO_5^{-\bullet}$ radicals to explain the inhibitory effect through scavenging of radicals as in equation (53).

$$RCH_2OH + SO_5^{-\bullet} \longrightarrow RCHO + SO_4^{-\bullet} + H_2O \qquad (53)$$

The effect of alcohols has been studied on several catalysed S(IV) autoxidation by Gupta et al.,(2008[54]). Gupta et al (2000[37]) studied the effect of Ag (I) catalyzed autoxidation of S(IV) in acetate buffer medium. To explain the observed kinetics and inhibition effect of organic compounds, the following general radical mechanism involving $SO_3^{-\bullet}$, $SO_4^{-\bullet}$ and $SO_5^{-\bullet}$ radicals was proposed (Backstrom, 1934[74]). Further experiments were conducted for finding reactivity of oxysulphur radicals with organics, which proved that these compounds react with $SO_4^{-\bullet}$ (Ashmore, 1963[97] Gilvert et al., 1988[98] Dogliotti and Hayon, 1967;[99] Clifton and Huie, 1989[100]). The reactions with $SO_3^{-\bullet}$ and $SO_5^{-\bullet}$ appeared to be quite slow and hence unimportant (Hayon et al., 1972)[75]. These studies have shown the reaction of $SO_4^{-\bullet}$ to be very fast. Therefore, to explain the inhibiting effect, the following step has been proposed.

$$SO_4^{-\bullet} + C_2H_5OH \longrightarrow \text{non chain product} \qquad (54)$$

From the above discussion, it is this apparent that to understand the mechanism of SO_2 oxidation it is necessary to study the effect of inhibitors. There are some reactions for which mechanisms involving complex formation alone or combined with radicals may be operating depending up on the reaction conditions in particular pH. For example iron (III)-catalysed reaction in the pH range(1-3) is without any effect of free radical scavengers but is strongly inhibited when pH>5 (Martin, 1984[24]). In addition, aqueous phase concentration of methanol and ethanol were found 1.8×10^{-6} mol dm^{-3} and 3.1×10^{-7} mol dm^{-3} respectively in urban atmosphere (Herrmann et al, 2000)[87] The Concentration of benzene reported to be 1.7 ppb in the atmosphere (Bravo, 2002)[88]

Experimental studies on the kinetics and products of sulphate radicals-alcohols (Clifton and Huie 1989[100] wine at el 1989[101] Ziajka et al 1996[102], 2001[103], Ziakjka and Pasiuk-Bronokowska 1998[83], 2000[104] 2003[91]) have also been carried out. The methanol inhibition of the uncatalysed autoxidation of HSO_3^- was investigated by Connick et al (1995)[67]. The inhibition by methanol in the Manganese (II) catalysed S (IV) autoxidation has been studied by Connick and Zhang (1996)[38]

Recently Gupta et al, 2008[54] studied the inhibiting effect of ethanol on CoO, Co_2O_3 and Ni_2O_3 catalysed autoxidation of S (IV) in alkaline medium and based on the result a radical mechanism for CoO and Co_2O_3 catalysis in alkaline medium, and non –radical mechanism for Ni_2O_3 in both alkaline and acidic media and for CoO in acidic media proposed. Similarly Sameena, Faiyaz and Prasad el al studied on kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium and free radical mechanism proposed. (2013)[105] In the same series the influence of VOCs on the oxidation of S(IV) by oxygen and role of some organic inhibitors on the oxidation of S(IV) by oxygen in rain water medium studied by Dhayal Chandel and Gupta et al (2014)[106-107]

10 PURPOSE AND SCOPE OF THE PROPOSEDWORK

Based on the literature survey and studies carried out so far, it is well established that the organic inhibitors have played a key role in the chemistry of acid rain. Further, it is fully realized that the role of inhibitors owing to their radical scavenging ability is a major diagnostic tool for the reaction mechanisms. Although the role of different moieties, ammonia and ammonia based derivatives are well studied. Among the inhibitors, the role of Formic acid, Aniline, Benzamide, Isoamyl alcohol, sodium benzoate, Isopropyl alcohol has not been studied so far in S(IV) autoxidation reaction. In view of the fact that inhibitor help in delineating the mechanism of autoxidation, whether radical or non-radical, it has been decided to study the effect of Formic acid, Aniline, Benzamide, Isoamyl alcohol, sodium benzoate, Isopropyl alcohol on the autoxidation rates of S(IV). This study will be beneficial to understand the related mechanism.

10.1 Importance of Proposed Research Work

This study is important in understanding the mechanism of the atmospheric oxidation of S(IV) by O_2 and the role of organic compounds which acts as inhibitors, many of which are found in atmosphere in trace amounts. It is useful to understanding rain water acidity and atmospheric chemistry. The main goal of this work is to determine rate constants for effect of organic compounds on sulphate radicals in order to shed some light on these reactions.

REFFERENCES

1. F. Dentener , B. Ervens, C. George, J. E. Williams, G. V. Buxton, G. A. Salmon, M. Bydder, F. Wilkinson, P. Mirabel, R. Wolke, H. Herrmann, 2003, CAPRAM 2.4 (MODAC mechanism) an extended and condensed tropospheric aqueous phase mechanism and its application. *J. Geophys. Res.* ***108,*** 4426. doi:10.1029/2002JD002202.
2. Acker K, Moller D, Wieprecht W, Auel R, Kalass D and Tscherwenka W, 2001, Nitrous and nitric acid measurements inside and outside of clouds at mt. Brocken *water air and soil pollution,* **130**, 331-336.
3. Acker K, Moller D, Wieprecht W, Auel R, Kalass D and Tscherwenka W, 2005, concentrations of nitrous acid, nitric acid, nitrite and nitrate in the gas and aerosol phase at a site in the emission zone during ESCOMPTE 2001 experiment, *atmospheric research,***74**, 507-524.
4. Brimblecombe P., Spedding D.J., 1974, The reaction order of the metal ion catalysed oxidation of sulphur dioxide in aqueous solution. *Chemosphere,* **1**, 29-32.
5. Da-Jiongling, Qian Chun Huang Ying Ouyang, 2010, Impacts of simulated acid rain on soil enzyme activities in a latosol, *Ecotoxicology and Environmental safety,* 73, **8**, 1914-1918.
6. Elissa Franzoni, Enrico Sassoni, 2011, Correlation between micro structural characteristic and weight loss of natural stones exposed to simulated acid rain, *Science of the total environment,* **412**, 278-285.
7. Kulshrestha U.C., Sarkar A.K., Srivastava S.S., Parashar D.C., 1995, Wet-only and bulk deposition studies at New Delhi (India), *Water Air and Soil Pollution,* **85**, 2137-2142.
8. Kulshrestha U.C., Sarkar A.K., Srivastava, S.S., Parashar, D.C., 1996, Investigation into atmospheric deposition through precipitation studies at New Delhi (India), *Atmospheric Environment,* **30**, 4149-4154.
9. Kulshrestha U.C, Kulshrestha M.J., Sekhar R, Sastry G.S. R., Vairamani M, 2003, Chemical characterization of rain water at an urban site of south Central India, *Atmos. Environ*., **37 (I)** 3019-3026.

10. Banerjee D., 2008, Study of precipitation chemistry over an industrial city, *Int J Environ Sci. tech*, **5 (3)** , 331-338.
11. Saxena P, Turpin B.J., Andrews E., 2000, Measuring and simulating particulate organics in the atmosphere problems and prospects. *Atmospheric Environment*, **34**, 2983–3013.
12. Khemani L.T., Momin G.A., Naik M.S., Prakasa Rao P.S., Kumar R., Ramana Murty Bh.V., 1985a, Trace elements and sea salt aerosols over the sea areas around the Indian Sub Continent, *Atmospheric Environment,* **19**, 277.
13. Khemani L.T., Momin G.A., Naik M.S., Prakasa Rao P.S., Kumar R., Ramana Murty Bh.V., 1985b, Impact of alkaline particulates on pH of rain-water in India, *Water Air and Soil Pollution*, **24**, 365.
14. Gupta K. S., Bhargava P., Manoj S. V. and Bhargava R., 2000, Kinetics and mechanism of silver(I) catalyzed oxidation of aqueous sulphur(IV) in acetate buffered medium, *Transition Metal Chemistry***, 25**, 329-332.
15. A. J. Franck, F. Turecek, 1999, Study of Sulpfur oxidation product by pyrolysis high resolution mass spectrometer *Eur. Mass spectrum,* **5**, 375-384.
16. Lee Y. J. and Rochelle G. T., 1987, Oxidative degradation of organic acid conjugated with sulfite oxidation in flue gas desulphurization: products, kinetics and mechanism, *Environment Science and Technology,* **21**, 266-271.
17. Brandt C. and van Eldik R., 1995, Transition metal catalyzed oxidation of aqueous sulphur(IV) oxides, Atmospheric Relevant Process and Mechanisms**,** *Chemical Reviews,* **95**, 119-190.
18. Calvert J. G. and Stock well W. R., 1984, Mechanisms and rates of sulphur dioxides in atmosphere, In: *SO_2, NO and NO_2 Oxidation Mechanisms. Atmospheric Considerations,* J. G. Calvert (Ed.), Butterworths, Boston, pp 1-62.

19. Hoffman M R and Edwards J O, 1975, Kinetics of the oxidation of sulphite by hydrogen peroxide in acidic medium, *journal of physical chemistry*, **79**, 2096-2098.
20. Halperin J and Taube H, 1952, The transfer of oxygen atoms in oxidation reductions IV The reaction of hydrogen peroxide with sulfite and Thiosulphate and of oxygen, MnO_2 and of MnO_4^- with sulfite, *J American Chemical Soc.*, **74**, 375-380.
21. Penkett S.A., Jones B.M.R., Eggleton A.E.J.1979, A study of SO_2 oxidation in stored rainwater samplers, *Atmos. Environ.* **13**, 139–147.
22. Penkett S.A., Jones B.M.R., Brice K.A., Eggleton A.E.J., 1979, The importance of atmospheric ozone and hydrogen peroxide in oxidising sulphur dioxide in cloud and rain-water, *Atmospheric Environment,* **13**, 123.
23. Larson T.V., 1976, The kinetics of sulphur dioxide oxidation by oxygen and ozone in atmospheric hydrometers, Ph.D. Thesis, University of Washington.
24. Martin L. R., 1984, In *SO_2, NO and NO_2 Oxidation Mechanisms, Atmospheric Considerations*, Calvert J. G. (Ed.), Butterworth, Boston**.** pp 63-100.
25. Hoffman M. R. and Jacob D. J., 1984, In *SO_2, NO and NO_2 Oxidation Mechanisms, Atmospheric Considerations,* Calvert, J.G. (Ed.), Butterworth, Boston, pp 101-172.
26. Hoffmann M. R. and Boyce S. D., 1983, In *Trace Atmospheric Constituents, Properties, Transformations and Fates*, S. E. Schwartz, (Ed.), John Wiley and Sons, New York, pp 147-189.
27. Kraft J. and Van Eldik R., 1989, Kinetics and mechanism of the iron(III)-catalyzed autoxidation of sulphur(1V) oxides in aqueous solution formation of transient iron(III)- sulphur(1V) complexes, *Inorganic Chemistry,* **28**, 2297-2305.

28. Kuo D. T. F., Krik D. W. and Jia C. Q., 2006, The chemistry of aqueous S(IV)-Fe-O_2 system, state of the art, *Journal of Sulphur Chemistry*, **27**, 461-530.

29. U. Schurath, J. Peeters, R. P. Wayne, G. K. Moortgat, I. Grgic, C. George, H. Herrmann, D. Poppe, 2003, *Towards Cleaner Air for Europe – Science, Tools and Applications Part 2, Overviews from the Final Reports of the EUROTRAC-2 Subprojects* (Eds P. M. Midgley,M. Reuther), pp. 73–98.

30. Manoj S. V., Mishra C. D., Sharma M., Rani A., Jain R., Bansal S. P. and Gupta K. S., 2000, Iron, manganese and copper concentrations in wet precipitations and kinetics of the oxidation of SO_2 in rain water at two urban sites Jaipur and Kota in Western India, *Atmospheric Environment,* **34**, 4479-4486.

31. Fuzzi S., 1978, Study of iron(III) catalyzed sulphur dioxide oxidation in aqueous solution over a wide range of pH, *Atmospheric Environment*, **12,** 1439-1442.

32. Brimblecombe P., Spedding D.J., The Catalytic oxidation of micro molar aqueous S(IV), *Atmospheric Environment,* **8**, 937-945.

33. Conklin M. H. and Hoffmann M. R., 1988, Metal ion-sulphur(IV) chemistry, 3, Thermodynamics and kinetics of transient iron(III)-sulphur (IV) complexes, *Environ. Sci. Technol.* **22**, 899–907.

34. Huss Jr. A., Lim P. K. and Eckert C. A., 1982, Oxidation of aqueous sulphur dioxide, Homogenous manganese(II) and iron (II) catalysis at low pH, *Journal of Physical Chemistry* ,**86**, 4224-4228.

35. Wilkosz I., Konieczynski J., Zajusz-Zubek E. 1999, Kinetic studies of S(IV) catalytic oxidation in aqueous solutions at concentrations close to those found in the atmosphere, *Arch Environ Prot.*, **25**, 51–52.

36. I. Grgic R. Losno, W. Pasiuk-Bronikowska, in *EUROTRAC-2 CMD Final Report, 2003, part III-1* (Eds U. Schurath,K.-H. Naumann).

37. Manoj S.V, Gupta K.S. and Bhargava P., 2000, Kinetics of tetra ammine copper(II) catalysed oxidation of sulphur(IV) by peroxydisulphate in ammonia buffer, *Transition Metal Chemistry,* **25**, 274-278.

38. Connick R.E., Zhang Y.-X., 1996, Kinetics and mechanism of the oxidation of HSO_3^- by O_2, The manganese(II)-catalyzed reaction. *Inorg. Chem.* **35**, 4613–4621.

39. Berglund J., Fronaeus S., Elding L.J., 1993, Kinetics and mechanism for manganese-catalyzed oxidation of sulphur(IV) by oxygen in aqueous solution, *Inorg. Chem,* **32**, 4527–4538.

40. Podkrajsek B., Grgic I. and Tursic J., 2002, Determination of sulphur oxides formed during the S(IV) oxidation in the presence of iron, *Chemosphere,* **49**, 271–277.

41. S. Lunak, A.M. El-Wakil and J. Veprek-Siska, 1978, Autoxidation of sulphite catalysed by 3d transition metals and inhibited by 2-propanol mechanism of inhibited and induced reactions Coll, *Czech. Chem. Commun.,* **43**, 3306.

42. Fuller E.C. and Crist R.H., 1941, The rate of oxidation of sulfite ions by oxygen, *J American chemical Soc.,* **63**, 1644-1650.

43. Hobson D.B. Richardson P.J. and Robinson P.J., 1986, Kinetics and mechanism of Co Catalysed reaction of oxygen and sulfite at very low concentrations, *J of Chem Soc*. Faraday Transactions 1, **82,** 869-881.

44. R.D. Srivastava, A.F. McMillan and I.J. Harris, Can. J. Chem., 1968, The kinetics of oxidation of sodium sulfite, *J of chemical Engineering,* **46**, 181.

45. Gupta K.S., Bhargava P. and Manoj S.V., 1999, Kinetics of silver(I) catalysed oxidation of sulphur(IV) by peroxodisulfate, *Indian Journal of Chemistry,* **38A**, 692-697.

46. Gupta K.S., Bhargava P. and Manoj S.V., 2001, Kinetics of diamminesilver (I)-catalysed oxidation of sulphur(IV) by dioxygen in ammonia buffers, *Transition Metal Chemistry***,** **26**, 71-75.

47. Gupta K. S., Jain U., Singh A., Mehta R. K., Manoj S. V., Prasad D. S. N., Sharma A., Parashar P., Bansal, S. P., 2004, Kinetics and mechanism of the osmium (VIII)-catalysed autoxidation of aqueous sulphur dioxide in acidic and alkaline media, *Journal of Indian Chemical Society,* **81**, 1083-1092.

48. D.E. Linn Jr., M.J. Dragan and D.E. Miller, 1990, Catalysis of autoxidation of aqueous sulphur dioxide using [Ni^{III}(cyclam)] evidence for a novel radical chain mechanism, *Inorg. Chem.*, **29**, 4356.

49. Pasuik-Bronikowska W. Bronikowski, T. and Ulejczyk M., 1997, Solubilization of organics un water coupled with sulfite Autoxidation, *Water Research*, **31**, 1767-1775.

50. Rani A., Prasad D. S. N., Madnavat P. V. S., Gupta K. S., 1992, The role of free fall atmospheric dust in catalysing autoxidation of aqueous sulphur dioxide, *Atmospheric Environment*, **26A**, 667-673.

51. Prasad D. S. N., Rani A., Gupta K. S., 1992, Surface-Catalyzed oxidation of Sulphur(IV) in Aqueous silica and copper(II) oxide suspensions, *Environmental Science and Technology,* **26,** 1361-1368.

52. Bhargava R., Rani A. and Gupta K. S., 1993, Oxidation of aqueous sulphur dioxide in suspensions of magnesium dioxide, Removal of SO_2 from flue gases, *Indian Journal of Chemistry*, **32A,** 713-716.

53. Rani A., Prasad D. S. N., Jain U. and Gupta K. S., 1991, Dynamics of multiphase glass powder catalysed autoxidation sulphur dioxide in bulk in aqueous phase, *Indian Journal of Chemistry*, **30A**, 756-764

54. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., 2008, Kinetics of the uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 Catalyzed autoxidation of Sulphur(IV) in alkaline medium, *Transition Metal Chemistry,* **33**, 809-817.

55. Prasad D. S. N., Rani A., Madnavat P. V. S., Bhargava R. and Gupta K. S., 1991, Kinetics of surface catalyzed oxidation of sulphur(IV) by dioxygen in aqueous suspensions of cobalt(II) oxide, *Journal of Molecular Catalysis*, **69**, 395-405.

56. Gupta K. S., Singh R., Saxena D., Manoj S. V. and M. Sharma, 1999, Role of manganese dioxide in the autoxidation of sulphur(IV) in toxic and anoxic suspensions, *Indian Journal of Chemistry***,** **38A**, 1129-1138.

57. Bhargava R., Prasad D. S. N., Rani A., Bhargava P. Jain U. and Gupta K. S., 1992, Kinetics of autoxidation of aqueous sulphur dioxide in suspensions of nickel(III) oxide, *Transition Metal Chemistry*, **17**, 238-241

58. Manoj S.V., Sharma M. and Gupta K.S. 1999, Role of cuprous oxide in autoxidation of aqueous sulphur dioxide and its atmospheric implications, *Atmospheric Environment*, **33,** 1503-1512.

59. Prasad D. S. N., Mehta R. K., Parashar P., Madnawat P. V. S., Rani A., Singh U., Manoj, S. V., Bansal S. P. , Gupta K. S., 2003, Kinetics of surface-catalysed autoxidation of aqueous sulphur dioxide in cobalt(III) oxide suspensions, *Journal of Indian Chemical Society*, **80**, 391-394.

60. Cohen S, Chang S.G. Markovitz S S and Novakov T., 1981 Role of fly ash in catalytic oxidation of S (IV) slurries, *Environmental Sc. And tech*. **15**, 1498-1502.

61. Madnavat P.V.S., Rani A., Sharma M. Prasad D.S.N., and Gupta K.S., 1993, Role of surface and leached metal ion catalysis in autoxidation of S(IV) in power plant flyash suspensions, *Atmospheric environment,* **27A,** 1985-1991

62. Saxena D., Sharma M., Rani A. and Gupta K.S. 1995, studies on rates of autoxidation of aqueous sulphur dioxide in several fly ash suspensions. Implications for acid rain, *J Environment Sc. And Health,* **A-30**, 1191-1210.

63. Brodzinsky R, Chang SG, Mankovitz SS, Novakov T, 1980, Kinetics and Mechanism of catalytic oxidation of sulphur di oxide on carbon in aqueous suspension, *J of physical chemistry,* **84**, 3353-3358.

64. Gupta K.S., Madnawat P.V.S., Bhargava R., Prasad D.S.N., Sharma M. rani A, 1992, Autoxidation of Aqueous Sulphur di oxide in suspensions of minerals and rocks, precip, scavenging *atmos-surf-exch,* 153-160.

65. Saxena D., Sharma M., Rani A., Singh R, Gupta K.S., 1993, Kinetics of oxidation of aqueous Sulphur di oxide by lead dioxide in aqueous suspensions, *Indian Journal of environmental protection,* **15**, 575-579.

66. Prasad D. S. N., Rani A., Sharma M. and Gupta K. S., 1994, Rates of autoxidation of sulphur(IV) in aqueous suspensions of limestone powder, Implications for scrubber chemistry, *Indian Journal of Chemistry*, **1**, 87-92.

67. R.E. Connick, Y.X. Zhang, S. Lee, R. Adamic and P. Cheing, 1995, kinetics and mechanism of oxidation of HSO_3^- by O_2 the uncatalysed reactions, *Inorg. Chem*., 34, 4543.

68. Berresheim H, Talbot R.W., Andreae M.O., Jacob D.J., Beecher, K.M., 1990, Source and sink of formic and acetic, and pyruvic acids over central Amazon, *Journal of Geophysical Research*, **95**, 16799–16811.

69. Huss A., Jr. Lim P. K. and Eckert C. A., 1978, On the ‘uncatalyzed’ oxidation of sulphur(IV) in aqueous solutions, *Journal of American Chemistry Soc*iety, **108**, 6253.

70. Huss Jr. A. Lim, P. K. and Eckert, C. A., 1982, Oxidation of sulphur dioxide, High pressure studies and proposed reaction mechanisms, *Journal of Physical Chemistry*, **86**, 4229-4233.

71. Huss Jr. A, Lim P. K. and Eckert C. A., 1982, Oxidation of sulphur dioxide, The effects of chelating agents and phenolic antioxidants, *Journal of Physical Chemistry*, **86**, 4233-4237.

72. Huie R. E. and Peterson, N. C., 1983, In *Trace Atmospheric Constituents, Properties, Transformations & Fates*, S. E. Schwartz, (Ed.), John Wiley and Sons, New York**,** pp 118-143.

73. Huie R. E. and Neta P., 1984, Chemical behaviour of SO_3^- and SO_5^- radicals in aqueous solutions, *Journal of Physical Chemistry*, **23**, 5665-5669

74. Backstrom H. L. J., 1934, The chain mechanism of the autoxidation of sodium sulfite solutions, *J. Phys. Chem.*(B), **25**, 122-138.

75. Hayon E., Treinin A. and Wilf J., 1972, Electronic spectra, photochemistry and Autoxidation mechanism of the sulfite-bisulfite pyrosulfite systems. The SO_2^-, SO_3^-, SO_4^- and SO_5^- radicals, *Journal of American Chemical Society*, **94**, 47-57.

76. Manoj S.V., Mudgal P.K. and Gupta K.S., 2008, Kinetics of iron (III) catalysed autoxidation of S(IV) in acetate buffered medium, *Transition meat chemistry,* **33**, 311-316.

77. Altwicker E. R., 1980, In *Advances in Environmental Sciences and Engineering,* Vol. **3.** J. R. Pfaffin and E. N. Zieglar (Eds.), Gordon and Breach Science Publishers, New York, pp 80-91.

78. Lee Raja, S. Raghunathan, R. Yu, X.-Y. T., Chen J., Kommalapati, R.R., Murugesan, K., Shen X., Qingzhong Y., Valsaraj K.T., Collett Jr. J.L., 2008, Fog chemistry in the Texas–Louisiana Gulf Coast corridor, *Atmos. Environ.* **42**, 2048–2061.

79. Grgic I., Dovzan A., Bercic G., and Hudnik V., 1998, The effect of atmospheric organic compound son the Fe-catalyzed S(IV) autoxidation in aqueous solution, *J. Atmos. Chem.* **29**, 315–337.

80. Podkrajsek B., Grgic I., and Tursic J., 2002, Determination of sulphur oxides formed during the S(IV)oxidation in the presence of iron, *Chemosphere* **49**, 271–277.

81. Ziajka J., Beer F. and Warneck P., 1994, Iron-catalyzed oxidation of bisulfite aqueous solution: Evidence for a free radical chain mechanism, *Atmospheric Environment,* **28(15)**, 2549-2552.

82. W. Pasiuk-Bronikowska, J. Ziajka, T. Bronikowski, 1992, *Autoxidation of Sulphur Compounds,* (Ellis Horwood: New York).

83. J. Ziajka, W. Pasiuk-Bronikowska, 1998, Effect of α- pinene and Cis-verbenol on the rate of S (IV) oxidation catalysed by Fe, Proceedings of EUROTRAC symposium 98 Transport and chemical transformation in the troposphere, Gramisch Partenkirchen Germany, 756-764.

84. Pasuik-Bronikowska, W. Bronikowski, T. Ulejczyk, M., 1998, Chemical interactions of aqueous phase pollutants, Sulphur dioxide and sobrerol in U. Schurath and R. Roselieb (Eds.), Proc. 2nd Workshop of the EUROTRAC-2 Subproject Chemical Mechanism Development, Forschungszentrum Aachen, Aachen, pp. A12, 1-4.

85. Pasuik-Bronikowska W., Bronikowski, T., Ulejczyk, M., 2000, Transformation of atmospheric constituents and pollutants induced by S(IV) Autoxidation. Chemistry and kinetics. In: EUROTRAC-2 Annual Report, CMD Chemical Mechanism Development, ISS, Munich, pp 123-126.

86. Rudzinski K. A. and Pasuik-Bronokowska, Isoprene inhibition of S(IV) autoxidation initiated by peroxydisulfate, In, *Transport and chemical Transformation in the Troposphere, Proc. EUROTRAC-2 Symp. 2000,* P. M. Midgley; M. J. Reuther and M. Williams (Eds.), Springer, Berlin, pp 1-4.

87. Herrmann H., Ervens B., Jacobi H.W., Wolke R., Nowacki P., Zellner R., 2000, A chemical aqueous phase radical mechanism for tropospheric chemistry, *Journal of Atmospheric Chemistry*, **36**, 231–3284.

88. Bravo H, 2002, Concentration of Benzene and toluene in the atmosphere of southwestern area at Mexico city metropolitan zone, atmospheric environment, **36**, 3843-3849.

89. Bigelow S. L., 1988, Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.

90. Alyea H. N. and Backstrom H. L. J., 1929, The inhibitive action of alcohols on the autoxidation of sodium sulfite. *Journal of American Chemical Society*, **51**, 90-107.

91. Ziajka J and Pasiuk-Bronikowska W, 2003, Fe Catalysed autoxidation of S (IV) inhibited by aliphatic alcohols, nonterlinic and substituted with α-pinene skeleton, In proceedings of the joint workshop EC cluster 3 Chemical process and Mechanism. EC shaping of the future of atmospheric chemistry research in Europe, University of Paris, Paris.

92. Wolf A., Deutsch F., Hoffmann P. and Ortner H. M., 2000, The influence of oxalate on Fe-catalyzed S(IV) oxidation by oxygen in aqueous solution, *Journal of Atmospheric Chemistry*, **37**, 125-135.

93. Pasuik-Bronikowska W., Bronikowski T., Ulejczyk M., 1999, Oscillations in the rate of S(IV) autoxidation inhibited by sobrerol, in R. Vogt and G.

Axelsdottir (Eds.), Proc. Joint Workshop, Ford Forschungszentrum Aachen, Aachen, pp. 195-198.

94. W. Pasiuk-Bronikowska, T. Bronikowski, M. Ulejczyk, 2003, Inhibition of the S(IV) autoxidation in the atmosphere by secondary terpenic compounds, *J. Atmos. Chem.*, ***44,*** 97. doi:10.1023/A:1022164702310.

95. Manoj S.V., Bhargava R., Rani A. and Gupta, K. S., 1992, Surface-mediated oxidation of aqueous sulphur dioxide in ceramic powder suspensions, *Indian Journal of Chemistry*, **31A,** 683-687.

96. Mudgal P.K., Bansal S.P. and Gupta K.S., 2007, Kinetics of atmospheric oxidation of nitrous oxide by oxygen in aqueous medium, *Atmospheric environment,* **41**, 4097-4105.

97. Ashmore P. G., 1963, *Catalysis and Inhibition of Chemical Reactions*. Butterworths, London.

98. Gilvert B. C., Stell J. K., Peet W. J. and Radford, K. J., 1988, Generation and reaction of the chlorine atom in aqueous solution, *Journal of Chemical Society, Faradey Transactions*, **1,** 84, 3319-3330.

99. Dogliotti L. and Hayon E., 1967, Flash photolysis of per sulfate ions in aqueous solution, Study of sulfate and ozonide radical anions, *Journal of Physical Chemistry,* **71**, 2511-2516.

100. Clifton C. L. and Huie, R. E. 1989, Rate constants for hydrogen abstraction reactions of the sulfate radical, SO_4^-, Alcohols, *International Journal of Chemical Kinetics,* **21,** 677-687.

101. Wine L Zhu, J. M. Nicovich, P. H., 2003, Temperature-dependent kinetics studies of aqueous phase reactions of SO_4^- Radicals with dimethylsulfoxide, dimethylsulfone, and methanesulfonate, *J. Photochem. Photobiol. Chem.*, ***157***, 311. doi : 10.1016/S1010-6030(03)00064-9.

102. J. Ziajka, P. Warneck, 1995, Reaction mechanism of the iron(III)-catalyzed autoxidation of bisulfite in aqueous solution, steady state description for benzene as radical scavenger. *Ber. Bunsenges. Phys. Chem., 99*, 59.

103. J. Ziajka W. Pasiuk-Bronikowska, 2003, Autoxidation of sulphur dioxide in the presence of alcohols under conditions related to the tropospheric aqueous phase, *Atmos. Environ,, **37***, 3913.

104. J. Ziajka W. Pasiuk-Bronikowska, 2005, Rate constants for atmospheric trace organics scavenging $SO_4^{-\bullet}$ in the Fe-catalysed autoxidation of S(IV). *Atmos. Environ., **39***, 1431.

105. Sameena Begam, faiyaz Huusain, D.S.N. Prasad, 2013, kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *pelagia research library*, **4**(1), 122-131 .

106. Yogpal Dayal, K,S, Gupta, 2014, Role of some organic inhibitors on oxidation of SO_2 in rain water medium, *Env. Sc. pollu Res*, vol. **21**, 3474 - 3483.

107. Yogpal Dayal, K.S. Gupta, 2014, The influence of hydroxyl organic compounds on the oxidation of SO_2 by oxygen, *Env. Sc. Pollu Res*, Vol **21**, 7808-7817

108. Anast J. M. and Margerum D. W., 1981, Trivalent copper catalysis of the autoxidation of sulfite, Kinetics and mechanism of the copper(III/II) tetraglycine reactions with sulfite, *Inorganic Chemistry*, **20**, 2319.

109. Clemitshaw, K. C. 2006, Coupling between the trophospheric photochemistry of nitrous acid (HONO) and nitric acid (HNO_3), *Environmental Chemistry*, **3**, 31-34.

110. Brandt C., Van Eldik R., 1995, Transition metal-catalyzed oxidation of sulphur(IV) oxides. Atmospheric relevant processes and mechanisms *Chemical Review*, **95**, 119–190.

111. Gupta K. S., 2002, Acid Rain Precursors, Sources Control and Damaging Effects, In: *Proceedings Second SERC School on Mathematical Modelling of Atmospheric Pollution,* Sapna Book House, Bangalore, pp.7-12.

CHAPTER - II

MATERIALS AND METHODS

In this Chapter the Source of Chemicals Catalysts, the Standardization Method and Procedure Adopted for following Reaction Kinetics have been Desired.

1. CHEMICALS

1.1 Sodium Sulphite

In aqueous solution, SO_2 exists as $SO_2.H_2O$, HSO_3^-, SO_3^{-2} and $S_2O_5^{-2}$ and all these forms collectively referred to as S(IV). In order to obtain aqueous solution of S(IV), sodium sulphite Na_2SO_3 (E. Merck) was used as such without any purification. Its solution was prepared in doubly distilled water. It was standardized iodometrically[1], every time before use. The solution was kept in refrigerator to prevent the autoxidation S(IV), which is considerably slow at low temperature.

1.2 Iodine

Iodine (E. Merck) of (99.9%) purity was used. To prepare 0.1mol L^{-1} solution of iodine at first 40.0 g iodate free potassium iodide (E. Merck 99%) was dissolved in 50 cm^3 of doubly distilled water, to which 25.5 g iodine was added. When iodine was fully dissolved the solution was made up to 1.0 liter. The stock solution was kept in cool and dark place. The dilute solutions of desired strength were prepared by diluting this stock solution.

1.3 Potassium Iodide

Iodate free potassium iodide (E. Merck, 99%) was used.

1.4 Silver Nitrate

Silver nitrate was prepared in chloride free doubly distilled water. It was E. Merck make (99.90%).

1.5 Sodium Thiosulphate

Sodium thiosulphate (Hypo) was E. Merck make and 99.90 % purity. Its stock solution was prepared by dissolving the weighed amount in freshly boiled doubly distilled water. The dilute solutions of desired strength were prepared by diluting this stock solution. The solution was standardized against iodine solution of known strength following the standard procedure (Jeffery et al, 1989)[2] A few drops of chloroform were added to the stock solution to prevent its slow decomposition.

1.6 Acetic Acid

For preparing 1.0 mol L^{-1} stock solution, 58 ml acetic acid (Merck 100%) was diluted with doubly distilled water. It was standardized by titrating against standard sodium hydroxide solution using phenolphthalein as an indicator.

1.7 Starch

For preparing indicator solution, starch (soluble) was used of Qualigens make.

1.8 Other Chemicals

The other chemicals used were of the following makes. Their solutions were prepared in doubly distilled water.

Table : 2.1

Qualities of some Chemicals Used

Chemicals	Make
Sodium Hydroxide (NaOH)	E.Merck (99.7%)
Sodium Acetate (CH_3COONa)	E.Merck (99.9%)
Copper Sulphate ($CuSO_4$)	E.Merck (99.9%)
Aniline($C_6H_5NH_2$)	E.Merck (99.9%)
Formic acid (HCOOH)	E.Merck (99.9%)
Sodium benzoate(C_6H_5COONa)	E.Merck (99.9%)
Benzamide($C_6H_5CONH_2$)	E.Merck (99.9%)
Isopropyl alcohol (C_3H_8O)	E.Merck (99.9%)
Isoamyl alcohol ($C_5H_{12}O$)	E.Merck (99.9%)

As the oxidation reactions of S (IV) are sensitive to the quality and source of chemicals[1], same reagents were used throughout the course of particular piece of work.

2. STANDARDIZATION METHODS

2.1 Iodine Solution

Iodine solution was standardized by taking its known volume in a flask, making it slightly acidic and titrating it against hypo solution using starch as indicator[2]

2.2 Sodium Thiosulphate (Hypo) Solution

It was standardized as follows. A known volume of standard copper sulphate was taken and to it potassium iodide was added. The liberated iodine was titrated against hypo using starch as indicator[2]

2.3 Sodium Sulphite Solution

A predetermined quantity of iodine which was always in excess over the sulphite to the estimated was taken in a conical flask and to it was added sodium sulphite solution to be standardized. Solution was made slightly acidic by adding acetic acid. The unreached iodine was titrated against hypo solution using starch as indicator[2]

2.4 Acetic acid Solution

It was standardized by titrating it against standard sodium hydroxide solution using phenolphthalein as an indicator[2]

3. EQUIPMENT

3.1 Reaction Vessel

The reactions were conducted in 0.15 L Erlenmeyer flask open to air and room light. The reaction vessel was placed in 0.5 L beaker provided with an outlet at the top and inlet at the bottom for circulating thermostatic water for maintaining the desired temperature of the reaction mixture ($\pm 1^{o}$C). The assembly was mounted on a magnetic stirrer.

3.2 pH meter

The digital pH meter (Systronics – pH system 361) was used for measuring the pH of the reaction mixture.

3.3 Magnetic Stirrer

The reaction vessel was mounted on a magnetic stirrer and the reaction mixture was continuously stirred magnetically at a speed of 1600±100 rpm for ensuring the rapid diffusion of oxygen in to reaction mixture and to keep the catalyst in solutions. The magnetic stirrer was calibrated with the help of Tachometer.

4. KINETICS PROCEDURE

The experimental procedure was exactly the same as described earlier by Brodzinsky et al (1980)[3] Mudgal et al (2008)[4] and Gupta et al (2008)[5] and is briefly given here. The all chemicals were used as reagent grade and solution were prepared in double distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature 30±1 ^{0}C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The selection of suitable stirring speed is necessary to save the reaction from becoming oxygen mass transfer controlled. For this reason, the rate of reaction were studied at different stirring speeds measured with the help of a tachometer (Mudgal et al, 2008)[4]. This led us to select a stirring speed of 1600±10 rpm for stirring the reaction mixture continuously and magnetically to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled.

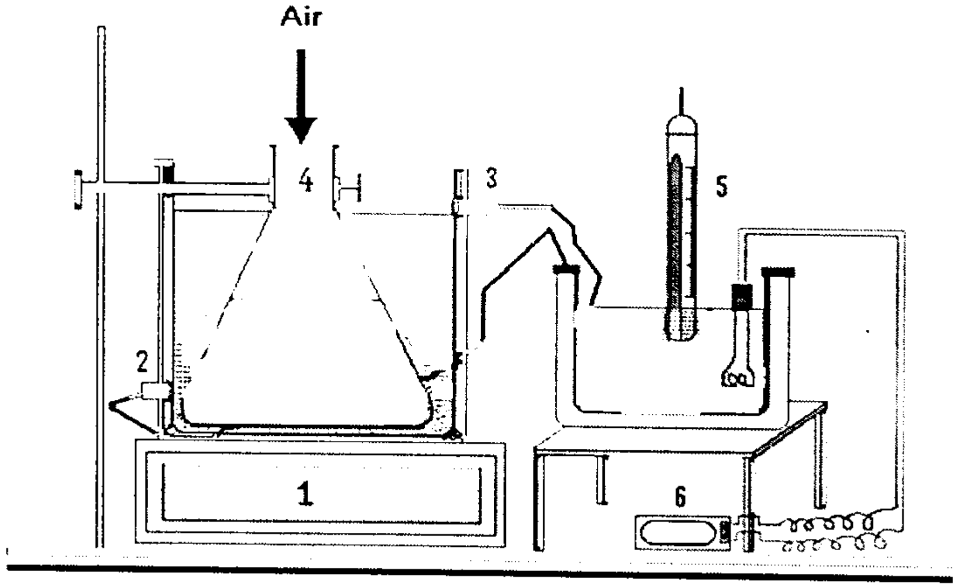


Figure 2.1: Schematic diagram of the experimental set up for the kinetic study of S (IV) – O_2 oxidation reaction. 1. Magnetic Stirrer, 2. Water Inlet, 3.Water outlet, 4. Erlenmeyer Flask (Reaction mixture), 5. Thermometer, 6.Thermostat.

The kinetics was studied in buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically in slightly acidic medium (Brodzinsky et al (1980)[3], Mudgal et al (2008)[4] , Prasad et al (1992)[6] and Gupta et al (2008)[5]. For this purpose 5.0 ml aliquot samples were withdrawn periodically and added to a titration flask containing known quantity of iodine and sufficient acetic acid to make medium acidic. The unreacted iodine was titrated with standard sodium thio sulphate solution using starch as an indicator.

5. TREATMENT OF KENETIC DATA

In this study, the treatment of kinetics is based on first order rate constants (k_{obs}) In case of Ag(I) catalysed autoxidation studies, the first order rate constants were calculated from the linear plots of log [S(IV)] v/s time. All calculations were performed in MS Excel 7.0

6. REPRODUCIBILITY

The S(IV) autoxidation rates are known to have only satisfactory reproducibility[3]. In our case, the duplicate rate determinations had a satisfactory reproducibility within 10%.

REFERENCES

1. A.I. Vogel, 1982, *A text book of quantitative Inorganic analysis* Longman Green, London, pp 357-370.
2. Jeffery G H, Basset J, Mendham J and Denney R.C., 1989, Vogles Textbook of Quantitative Chemical analysis, Addison Wesley Long man Limited Essex pp 383-385.
3. Brodzinsky R, Chang S.G., Mankovitz S.S., Novakov T., 1980, Kinetics and Mechanisms of the catalytical oxidation of sulphur dioxide on carbon in aqueous suspensions, *Journal of physical chemistry* **84,** 3353-3358.
4. Mudgal P.K., Sharma A.K., Mishra C.D., Bansal S.P. and Gupta K.S., 2008, Kinetics of ammonia and ammonium ion inhibition of the atmospheric oxidation of aqueous sulphur dioxide by oxygen, *Journal of atmospheric chemistry*, **61,** 31-55.
5. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., 2008, kinetics of uninhibited and ethanol inhibited CoO, Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Trans metal chem.*, **33**, 809-817 doi 10.1007/s 11243-008-9115-6.
6. D.S.N. Prasad, A. Rani and K.S. Gupta, 1992, *Environ. Sci. Technol.*, **26**, 1361, doi10.1021/es00031a013.

CHAPTER - III

Kinetics of Formic Acid Inhibited Uncatalysed and Ag (I) Catalysed Autoxidation of S (IV) in Acidic Medium

ABSTRACT

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. Based on the observed results a free radical mechanism operative and following rate law has been proposed.

$$-d\,[S(IV)/dt \quad = \quad (k_1+k_2[Ag])\,[S(IV)]/\,1 + \;B\,[\text{Formic acid}]$$

INTRODUCTION

A large number of organic and inorganic chemical species are released in to the atmosphere by anthropogenic and natural sources. The subsequent photochemical and thermal reactions of these species in gas and aqueous phase form the backbone of the atmospheric chemistry. The atmospheric reactions of SO_2 and NO_x etc. are major acid rain precursors and are responsible for acidification of various forms of atmospheric water. Studies in India and abroad have shown that anthropogenic sources in the atmosphere are the major contributors of SO_2 and NO_x which are transformed in to acids such as HNO_2, HNO_3, H_2SO_3 and H_2SO_4 (Calvert et al [1] Berresheim and Jaeschke[2]). Measurable quantities of low molecular weight (LMW) aldehydes and monocarboxylic acids are present in Los Angeles urban atmospheres (Grosjean 1982[3], 1983[4], Kawamura et al. 1985a[5], 2000[6]) and rural/remote atmosphere (Keene et al. 1983[7], Talbot et al. 1988[9], 1990[10], Khwaja 1995[8], Helas et al. 1992[11]). The compounds primarily originate from incomplete combustion of fossil fuels mainly by automobiles and secondarily from photochemical reactions of anthropogenic hydrocarbons and other precursors in the atmosphere (Kawamura et al. 1985b[13], Chebbi and Carlier 1996[14], Kawamura et al. 2000[17]).

Studies of rainwater composition showed that C1–C10 mono carboxylic acids, C2–C10 dicarboxylic acids and C1–C2 aldehydes are present in wet precipitation as major organic species (Kawamura et al. 1996[12]). Gupta et al 2000[15], studied the Ag (I) catalyzed autoxidation of S (IV) in acetate buffer medium and proposed a free radical mechanism. Since with the change in the pH, the mechanism of the reaction as well as the effect of free radical scavengers is known to change (Martin, 1984)[16], it is planned to study the kinetics of Ag (I) catalysed oxidation of S(IV) by O_2 in acidic medium in the presence of formic acid to examine its effect on the reaction rate.

EXPERIMENTAL

The experimental procedure was exactly the same as described earlier[29]. All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature $30 \pm 1\ ^{0}C$. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at 1600 ± 10 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically. The reproducibility of replicate measurements was generally better than 10 ± 1 %. All calculations were performed in MS Excel.

PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S(VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure.[29]

The product analysis showed the recovery of sulphate to be 98 ± 1%., in all cases in agreement with eq. (1)

$$S(IV) + 0.5\,O_2 \longrightarrow S(VI) \qquad (1)$$

RESULTS

Preliminary Investigation

The kinetics of both uncatalysed and Ag (I) Catalysed and formic acid inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30° C. In both the cases the first order dependence of S (IV) was observed in the kinetics data treatment for the determination of first order rate constant k_1 was carried out from log [S(IV)] versus time, t The plots were shown in fig 3.1. From the fig.3.1 observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by formic acid.

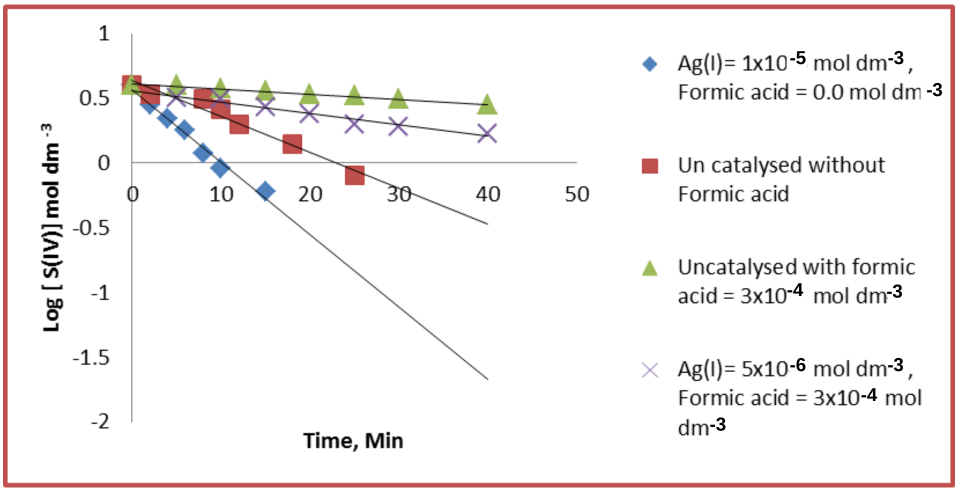


Fig. 3.1 : The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2x 10^{-3} mol dm^{-3} at pH = 4.95, t = 30° C

(◇) Ag (I) = 1x 10^{-5} mol dm^{-3}, (formic acid) = 0.0 mol dm^{-3}

(☐) Uncatalysed without formic acid

(△) Uncatalysed with formic acid = $3x10^{-4}$ mol dm^{-3}

(x) Ag (I) = 5x 10^{-6} mol dm^{-3}, (formic acid) = 3x 10^{-4} mol dm^{-3}

Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of Ag (I) and all the solutions were prepared in doubly distilled water.

Table - 3.1

Quantitative Analysis of Sulphate in Final Product Solution

10^3 [S(IV)] mol dm^{-3}	Ag (I) mol dm^{-3}	pH	10^3 [SO_4^{-2}] mol dm^{-3}	[SO_4^{-2}]/[S(IV)]	% of S(IV) recovery
5.0	0.00	4.95	4.90	0.980	98.0
5.0	$5x10^{-6}$	4.95	4.92	0.984	98.4
5.0	$1x10^{-5}$	4.95	4.95	0.990	99.0

Table- 3.2

Variation of [S (IV)] at pH = 4.95, t = 30 °C, $CH_3COONa = 7x10^{-2}$mol L^{-1} $CH_3COOH= 3x10^{-2}$mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	3	4
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot			
(0)	0.0	0.0	0.0	0.0
(2)	0.5	0.6	1.3	1.6
(8)	0.8	0.9	2.1	2.2
(10)	1.0	1.4	3.2	3.2
(12)	1.2	2.0	3.8	4.3
(18)	1.4	2.6	4.6	5.4
(25)	1.6	3.2	4.8	6.5
∞	2.0	4.0	6.0	8.0
(10^3) k_1 s^{-1}	**1.04**	**1.06**	**1.09**	**1.09**

Figures in parentheses denotes time in minutes.

Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range from $1x10^{-3}$ mol dm^{-3} to $4x10^{-3}$mol dm^{-3} at pH =

4.95, t = 30^o C in acetate buffered medium. The kinetics was found to be first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of first order rate constant k_1 are given in table - 3.3 The dependence of reaction rate on [S(IV)] follows the rate law (2)

$$-d[S(IV)]/dt = k_1 [S(IV)] \qquad (2)$$

Table- 3.3

The values of k_1 for uncatalysed reaction at different [S(IV)] at pH = 4.95, t = 30 °C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	$(10^3) k_1 s^{-1}$
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

[Formic acid] Dependence

The major aim of this study was to examine the effect of formic acid on the autoxidation of S(IV) in acetate buffer medium and varying the [Formic acid] from $5x10^{-6}$ mol dm^{-3} to $8x10^{-4}$mol dm^{-3}, we observed the rate of the reaction decreased by increasing [Formic acid] The results are given in table 3.4 However the nature of the [S(IV)] dependence in presence of formic acid did not change and remains first order. The first order rate constant k_{inh} in the presence of formic acid was defined by rate law (3)

$$-d[S(IV)]/dt = k_{inh} [S(IV)] \qquad (3)$$

The values of k_{inh} in the presence of formic acid decreased with increasing [Formic acid] are given in Table 3.5 which are in agreement with the rate law (4)

$$k_{inh} = k_1 / (1+B\,[\text{Formic acid}]) \qquad (4)$$

Where B is inhibition parameter for rate inhibition by formic acid. The equation (4) on rearrangement becomes

$$1/ k_{inh} = 1/ k_1 + B \text{ [Formic acid] } / k_1 \qquad (5)$$

In accordance with the equation (5) the plot of $1/ k_{inh}$ v/s [Formic acid] was found to be linear with non- zero intercept fig 3.2 The values of intercept ($1/ k_1$) and slope (B/ k_1) were found to be 3.03×10^7 mol dm^{-3}s and 9.1×10^2s at pH = 4.95, t = 30^o C from these values the value of inhibition parameter B was found to be 3.33×10^4 mol dm^{-3}

Table - 3.4

Variation of [Formic acid], at [S(IV)] = 2×10^{-3} mol dm^{-3}, pH = 4.95, t = 30^o C, $CH_3COONa = 7 \times 10^{-2}$ mol L^{-1}, $CH_3COOH = 3 \times 10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	**5×10^{-6}**	**8×10^{-6}**	**1×10^{-5}**	**3.5×10^{-5}**	**7.5×10^{-5}**	**1×10^{-4}**	**3×10^{-4}**	**5×10^{-4}**	**8×10^{-4}**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.0	1.2	0.7	0.4	0.3	0.0	0.0	0.0	0.0
(10)	1.4	1.5	1.0	0.5	0.5	0.2	0.2	0.0	0.0
(15)	1.9	1.9	1.3	0.7	0.6	0.4	0.4	0.1	0.0
(20)	2.2	2.5	1.5	0.9	0.9	0.8	0.6	0.3	0.1
(30)	2.7	2.8	1.8	1.1	1.3	1.0	0.7	0.4	0.2
(40)	3.1	3.0	2.2	1.5	1.5	1.2	0.9	0.5	0.2
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**0.98**	**0.76**	**0.57**	**0.38**	**0.26**	**0.19**	**0.15**	**0.07**	**0.03**

Figures in parentheses denotes time in minute

Table - 3.5

The values of k_{inh} at different [Formic acid] at pH = 4.95, t = 30° C, $CH_3COONa = 7x10^{-2}$ mol L^{-1} $CH_3COOH = 3x10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	10^3 k_{inh} s^{-1}	$1/k_{inh}$ s
0.00	1.09	917
$5.0x10^{-6}$	0.98	1020
$8.0x10^{-6}$	0.76	1316
$1.0x10^{-5}$	0.57	1754
$3.5x10^{-5}$	0.38	2632
$7.5x10^{-5}$	0.26	3846
$1.0x10^{-4}$	0.19	5263
$3.0x10^{-4}$	0.15	6667
$5.0x10^{-4}$	0.07	14286
$8.0x10^{-4}$	0.03	33333

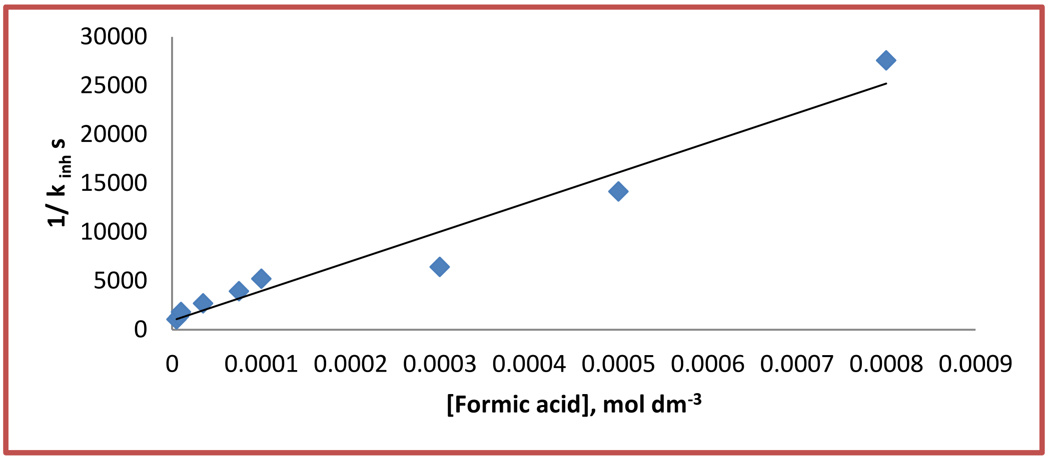


Fig 3.2 : Effect of formic acid at [S(IV)] = $2x10^{-3}$ mol dm^{-3} pH = 4.95, t = 30° C in acetate buffered medium

Ag(I) Catalysed Reaction

At first the kinetics of Ag(I) Catalysed reaction in the absence of inhibitor was studied.

[S(IV)] Variation

The dependence of S (IV) on reaction rate was studied by varying [S(IV)] from $1x10^{-3}$ mol dm^{-3} to $10x10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5x10^{-6}$ mol dm^{-3} and $1x10^{-5}$ mol dm^{-3} at pH = 4.95, t = 30^o C. The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in fig 3.1

Ag(I) Variations

The dependence of Ag(I) on the reaction rate was studied by varying Ag (I) from $5x10^{-6}$ mol dm^{-3} to $2.5x10^{-5}$ mol dm^{-3} at S(IV) = $2x10^{-3}$ mol dm^{-3} pH= 4.95, t= 30^o C in acetate buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig 3.3. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law– (6)

$$-d\,[S(IV)]\,/dt = k_{cat}\,[S(IV)] = (k_1+k_2[Ag(I)]\,[S(IV)] \qquad (6)$$

$$\text{Or} \qquad k_{cat} = k_1+k[Ag(I)] \qquad (7)$$

From the plot in fig 3.3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be 0.72x 10^1 s and 8.6 x 10^{-3} mol dm^{-3} respectively at pH = 4.95, t = 30^o C in acetate buffered medium.

Table- 3.6

Variation of [S(IV)] = $2x10^{-3}$ mol dm^{-3} at Ag (I) =$5x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.8	1.5	2.0	2.2
(4)	0.4	1.0	1.7	2.4	3.3	4.5
(6)	0.6	1.2	2.7	3.0	4.5	6.5
(8)	0.9	1.5	3.6	4.0	7.0	9.8
(10)	1.2	1.7	5.0	5.5	9.3	12.1
(15)	1.4	3.0	5.5	9.0	11.5	14.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**1.43**	**1.42**	**1.41**	**1.44**	**1.46**	**1.50**

Figures in parentheses denotes time in minutes

Table- 3.7

Variation of [S(IV)] = 2x10^{-3} mol dm^{-3} at Ag (I) =1x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10 ^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.9	3.0	4.5	5.6
(4)	0.8	1.8	2.8	4.8	6.3	7.8
(6)	1.2	2.2	3.6	5.9	7.8	9.5
(8)	1.4	2.8	4.5	7.8	8.9	10.2
(10)	1.5	3.1	5.0	8.9	12.5	12.8
(15)	1.7	3.4	7.0	10.3	13.6	17.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**2.19**	**2.15**	**2.15**	**2.18**	**2.14**	**2.10**

Figures in parentheses denotes time in minutes

Table- 3.8

Variation of Ag (I) at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}, CH_3COOH= $3\text{x}10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5\text{x}10^{-6}$**	**$1\text{x}10^{-5}$**	**$1.5\text{x}10^{-5}$**	**$2\text{x}10^{-5}$**	**$2.5\text{x}10^{-5}$**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.4	2.5	2.4
(4)	1.0	1.8	1.8	2.7	2.5
(6)	1.2	2.2	2.0	2.9	3.0
(8)	1.5	2.8	2.2	3.7	3.5
(10)	1.7	3.1	3.4		
(15)	3.0	3.4			
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.42**	**2.15**	**2.54**	**2.94**	**3.88**

Figures in parentheses denotes time in minutes

Table - 3.9

The values of k_{cat} at different concentration of Ag (I) mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1} CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	$10^3 k_{cat}$ s^{-1}
0.000005	1.42
0.00001	2.15
0.00015	2.54
0.00020	2.94
0.00025	3.88

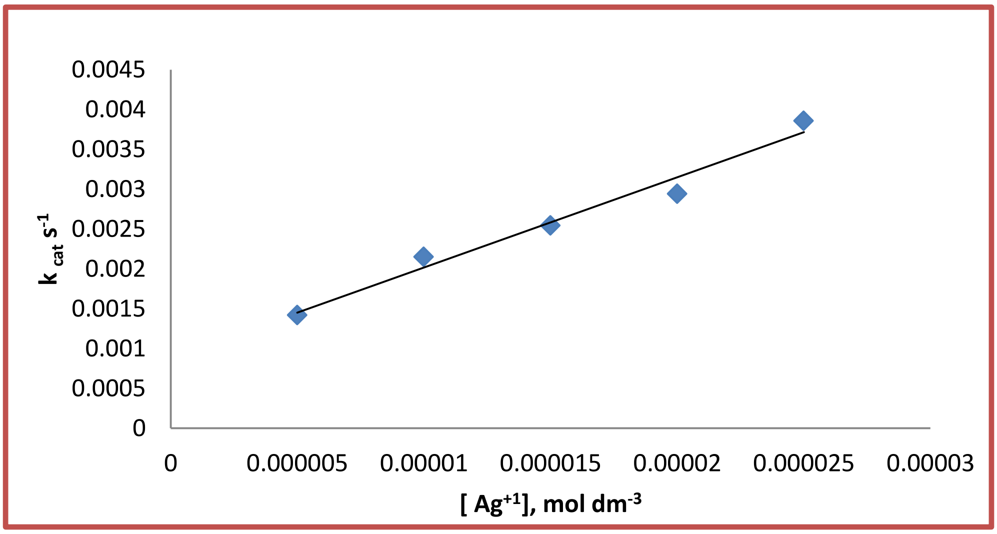


Fig.3.3 : The dependence of catalyst concentration at [S(IV)] = 2x10^{-3} mol dm^{-3} pH = 4.95, t = 30^o C in acetate buffered medium.

Variation of pH

Variation of pH was carried out from 4.02 - 5.25 at different [S(IV), Ag (I), [Formic acid] and temperatures. The rate decreases slightly by varying pH is inverse H^+ ion dependence was observed. From the plot of log k_1 v/s log (H^+) the order with respect to H^+ is 0.20 which is a fractional order and can be neglected as shown in fig 3.4

Table - 3.10

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3} [Formic acid] = 7.5x10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7x10^{-2}mol L^{-1}

pH	10 ^{3} k s^{-1}
4.02	0.315
4.35	0.365
4.56	0.426
4.75	0.469
4.95	0.491
5.25	0.553

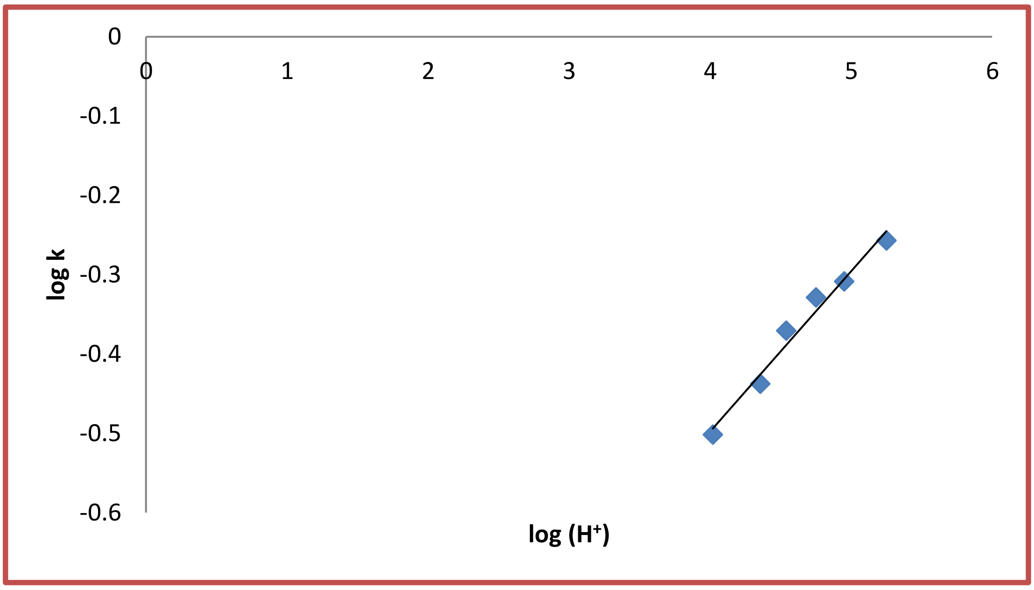


Fig. 3.4 : Effect of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, t= 30^{o} C in acetate buffered medium.

Table - 3.11

Rate of Ag (I) catalysed autoxidation in the presence of formic acid.

[Formic acid] mol dm^{-3}	**Ag (I) = 5x10^{-6} mol dm^{-3}**	**Ag (I) =1x10^{-5} mol dm^{-3}**	**Ag (I) =1.5 x 10^{-5} mol dm^{-3}**
pH = 4.02			
7.5 x 10^{-5}	0.253 x 10^{-3}	0.289 x 10^{-3}	0.314 x 10^{-3}
1.0 x 10^{-4}	0.055 x 10^{-3}		
3.0 x 10^{-4}	0.047 x 10^{-3}		
pH = 4.50			
7.5 x 10^{-5}	0.426 x 10^{-3}	0.488 x 10^{-3}	0.588 x 10^{-3}
1.0 x 10^{-4}	0.299 x 10^{-3}		
3.0 x 10^{-4}	0.267 x 10^{-3}		
pH = 5.25			
7.5 x 10^{-5}	0.553 x 10^{-3}	0.596 x 10^{-3}	0.695 x 10^{-3}
1.0 x 10^{-4}	0.425 x 10^{-3}		
3.0 x 10^{-4}	0.408 x 10^{-3}		

Table - 3.12

Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of formic acid.

[Formic acid] = 7.5 x 10^{-5} mol dm^{-3}	Ag (I) = 5x10^{-6} mol dm^{-3}	Ag (I) = 1 x 10^{-5} mol dm^{-3}	Ag (I) = 1.5 x 10^{-5} mol dm^{-3}
pH = 4.50			
	3.33	**4.44**	**4.32**

Table - 3.13

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5×10^{-6} mol dm^{-3}, [Formic acid] = 7.5×10^{-5} mol dm^{-3}, t= 30° C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.5	0.8	0.8	0.9	0.9	1.1
(10)	0.9	1.3	1.4	1.4	1.5	1.5
(15)	1.3	1.5	1.7	1.7	1.8	1.8
(20)	1.5	1.8	2.1	2.2	2.2	2.2
(25)	1.7	2.2	2.4	2.5	2.6	2.6
(30)	1.9	2.2	2.4	2.6	2.6	2.8
(40)	2.1	2.3	2.5	2.6	2.7	2.9
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.315**	**0.365**	**0.426**	**0.469**	**0.491**	**0.553**

Figures in parentheses denotes time in minutes

Table - 3.14

Variation of pH at [S(IV)] = 4x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.8	0.9	1.1	1.3	1.5	2.5
(10)	1.2	1.4	1.5	2.1	2.3	3.6
(15)	1.8	2.0	2.1	2.7	2.9	4.5
(20)	2.5	2.5	2.6	3.3	3.4	5.3
(25)	3.0	3.2	3.3	3.9	4.1	5.4
(30)	3.5	3.6	4.3	4.6	4.9	5.7
(40)	4.2	4.6	4.9	5.2	5.5	5.7
∞	8.0	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1, s^{-1}	**0.315**	**0.348**	**0.397**	**0.436**	**0.479**	**0.528**

Figures in parentheses denotes time in minutes

Table - 3.15

Variation of pH at [S(IV)] = 6x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	2.5	2.6	2.9	3.5	3.5	3.4
(10)	3.3	3.4	4.9	4.5	4.5	4.5
(15)	4.6	4.6	5.7	4.9	4.9	5.6
(20)	5.5	5.3	6.6	5.9	5.9	6.8
(25)	5.8	6.1	7.0	6.8	6.8	7.2
(30)	6.3	6.9	7.4	7.2	7.7	7.5
(40)	6.7	7.2	7.9	8.5	8.6	9.0
∞	12.0	12.0	12.0	12.0	12.0	12.0
(10^3) k_1, s^{-1}	**0.337**	**0.384**	**0.434**	**0.466**	**0.492**	**0.531**

Figures in parentheses denotes time in minutes

Table - 3.16

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 1×10^{-5} mol dm^{-3}, [Formic acid] = 7.5×10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.7	0.8	0.9	1.0	1.2	1.4
(10)	1.0	1.2	1.2	1.4	1.6	1.7
(15)	1.4	1.5	1.6	1.7	1.9	2.0
(20)	1.7	1.8	1.9	2.0	2.3	2.4
(25)	1.9	2.2	2.3	2.3	2.5	2.6
(30)	2.0	2.3	2.4	2.5	2.7	2.9
(40)	2.4	2.6	2.8	2.9	2.9	3.1
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.368**	**0.434**	**0.488**	**0.509**	**0.523**	**0.596**

Figures in parentheses denotes time in minutes

Table - 3.17

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 1.5×10^{-5} mol dm^{-3}, [Formic acid] = 7.5×10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3}mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.8	1.0	1.2	1.3	1.2	1.2
(10)	1.3	1.6	1.5	1.6	1.6	1.6
(15)	1.7	2.0	1.9	2.0	1.9	1.9
(20)	2.3	2.4	2.3	2.2	2.2	2.2
(25)	2.5	2.5	2.6	2.5	2.6	2.5
(30)	2.5	2.6	2.9	2.8	3.0	3.0
(40)	2.6	2.9	3.0	3.2	3.2	3.3
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.469**	**0.522**	**0.588**	**0.619**	**0.662**	**0.695**

Figures in parentheses denotes time in minutes

Table - 3.18

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Formic acid] = $1x10^{-4}$ mol dm^{-3}, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$ mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.2	0.3	0.7	0.8	0.8	0.8
(10)	0.2	0.5	0.9	0.9	1.0	1.4
(15)	0.5	0.7	1.2	1.2	1.2	1.5
(20)	0.7	1.2	1.4	1.4	1.5	1.8
(25)	0.9	1.4	1.5	1.8	1.8	2.0
(30)	1.2	1.4	1.7	1.8	2.3	2.4
(40)	1.3	1.7	2.2	2.3	2.4	2.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.179**	**0.242**	**0.299**	**0.329**	**0.385**	**0.425**

Figures in parentheses denotes time in minutes

Table - 3.19

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3} , [Formic acid] = 3x10^{-4} mol dm^{-3}, t= 30°C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.2	0.3	0.7	0.8	0.8	0.8
(10)	0.2	0.5	0.9	0.9	0.9	1.4
(15)	0.5	0.7	1.2	1.0	1.3	1.8
(20)	0.7	0.9	1.3	1.2	1.6	2.3
(25)	0.9	1.2	1.5	1.4	2.0	2.4
(30)	1.1	1.3	1.7	1.6	2.1	2.4
(40)	1.2	1.5	2.0	2.3	2.3	2.4
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.159**	**0.202**	**0.267**	**0.301**	**0.361**	**0.408**

Figures in parentheses denotes time in minutes

Table - 3.20

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, t= 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3}mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.5	0.6	0.8	0.9	1.0	1.2
(10)	0.8	0.9	1.3	1.2	1.2	1.6
(15)	1.1	1.2	1.5	1.5	1.4	2.0
(20)	1.4	1.4	1.8	1.9	1.5	2.1
(25)	1.5	1.7	2.0	2.0	1.8	2.2
(30)	1.8	2.0	2.3	2.5	2.2	2.9
(40)	2.3	2.6	2.7	2.9	3.3	3.3
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.338**	**0.407**	**0.441**	**0.510**	**0.596**	**0.659**

Figures in parentheses denotes time in minutes

Table - 3.21

Variation of pH at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = $5\text{x}10^{-6}$ mol dm^{-3}, [Formic acid] = $7.5\text{x}10^{-5}$ mol dm^{-3}, t= 40^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol cm^{-3} Hypo for 5 ml aliquot					
0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.7	0.8	1.0	1.2	1.3	1.2
(10)	1.0	1.3	1.3	1.5	1.6	1.6
(15)	1.3	1.5	1.7	2.0	2.0	2.4
(20)	1.6	2.0	2.0	2.2	2.4	2.9
(25)	2.0	2.2	2.3	2.5	2.8	3.0
(30)	2.2	2.3	2.5	2.8	3.0	3.0
(40)	2.5	2.6	2.8	3.0	3.0	3.3
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.408**	**0.432**	**0.487**	**0.564**	**0.605**	**0.733**

Figures in parentheses denotes time in minutes

Table - 3.22

Variation of [S(IV)] at Ag (I) = 5 x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.8	1.9	3.7	3	3.5
(10)	0.7	1.0	2.6	4.5	4.3	5.0
(15)	0.9	1.2	3.3	5.6	5.0	6.2
(20)	1.0	1.5	4.2	6.8	6.3	7.1
(25)	1.1	1.8	4.4	7.2	7.3	8.4
(30)	1.1	2.3	4.9	7.7	9.0	10.2
(40)	1.3	2.6	5.5	8.6	10.5	13.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.40**	**0.42**	**0.47**	**0.49**	**0.43**	**0.42**

Figures in parentheses denotes time in minutes

Table- 3.23

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$mol dm^{-3} , [Formic acid] = $7.5x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.8	2.1	3.8	3.2	3.4
(10)	0.7	1.0	2.9	4.9	4.7	5.4
(15)	0.9	1.2	3.6	5.7	5.4	6.8
(20)	1.2	1.5	4.4	6.8	6.7	7.9
(25)	1.3	2.0	5.2	7.2	7.9	8.7
(30)	1.3	2.6	5.2	7.9	9.4	10.9
(40)	1.4	2.9	5.8	8.8	11.8	15.1
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.54**	**0.53**	**0.53**	**0.51**	**0.51**	**0.52**

Figures in parentheses denotes time in minutes

Table- 3.24

Variation of [S(IV)] at Ag (I) =1.5 x10^{-5} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.9	2.5	3.9	3.2	4.2
(10)	0.7	1.2	3.5	4.8	4.5	6.3
(15)	0.9	1.5	4.2	5.9	5.6	8.4
(20)	1.2	1.6	4.9	6.8	6.7	10.2
(25)	1.4	1.9	5.9	7.3	7.8	12.2
(30)	1.4	2.9	6.2	8.3	9.8	14.6
(40)	1.5	3.2	6.2	9.5	12.8	15.8
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.63**	**0.64**	**0.66**	**0.60**	**0.60**	**0.66**

Figures in parentheses denotes time in minutes

Table - 3.25

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3} [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.3	0.3	0.3	0.3
(10)	0.7	0.7	0.7	0.7	0.7
(15)	0.9	0.9	0.9	0.9	0.9
(20)	1.0	1.2	1.1	1.2	1.2
(25)	1.1	1.3	1.2	1.4	1.4
(30)	1.1	1.3	1.4	1.4	1.5
(40)	1.3	1.4	1.5	1.5	1.6
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.40**	**0.54**	**0.60**	**0.63**	**0.72**

Figures in parentheses denotes time in minutes

Table - 3.26

Variation of Ag (I) at S(IV)] = 2 x10^{-3} mol dm^{-3} [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) **mol dm^{-3}**	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(5)	0.8	0.8	0.8	0.9	0.9
(10)	1.0	1.0	1.2	1.2	1.2
(15)	1.2	1.2	1.3	1.5	1.5
(20)	1.5	1.5	1.6	1.6	1.6
(25)	1.8	2.0	2.2	1.9	2.1
(30)	2.3	2.6	2.9	2.9	3.0
(40)	2.6	2.9	3.0	3.2	3.3
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.42**	**0.53**	**0.60**	**0.64**	**0.71**

Figures in parentheses denotes time in minutes

Table - 3.27

Variation of Ag (I) at S(IV)] = 4 x10^{-3} mol dm^{-3} [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(5)	1.9	2.1	2.5	2.5	2.5
(10)	2.6	2.9	3.2	3.5	3.6
(15)	3.3	3.6	4.0	4.2	4.4
(20)	4.2	4.4	4.4	4.9	5.2
(25)	4.4	5.2	5.2	5.9	6.0
(30)	4.9	5.2	5.5	6.2	6.4
(40)	5.5	5.8	6.2	6.2	6.6
∞	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1 s^{-1}	**0.47**	**0.53**	**0.59**	**0.66**	**0.75**

Figures in parentheses denotes time in minutes

Table- 3.28

Variation of formic acid at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) =5 $\times10^{-6}$ mol dm^{-3}, pH = 4.95, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH = 3×10^{-2} mol L^{-1}

[Formic Acid] mol dm^{-3}	**5×10^{-6}**	**8×10^{-6}**	**1×10^{-5}**	**3.5×10^{-5}**	**7.5×10^{-5}**	**1×10^{-4}**	**3×10^{-4}**
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.2	1.2	1.1	0.9	0.8	0.8	0.8
(10)	1.5	1.5	1.5	1.1	1.0	1.0	0.9
(15)	1.8	1.9	1.9	1.5	1.2	1.2	1.3
(20)	2.2	2.5	2.2	1.8	1.5	1.5	1.6
(25)	2.8	2.8	2.5	2.0	1.8	1.8	2.0
(30)	3.0	3.0	2.9	2.5	2.3	2.3	2.1
(40)	3.3	3.2	3.0	2.9	2.6	2.4	2.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.72**	**0.69**	**0.59**	**0.51**	**0.42**	**0.38**	**0.36**

Figures in parentheses denotes time in minute

Table - 3.29

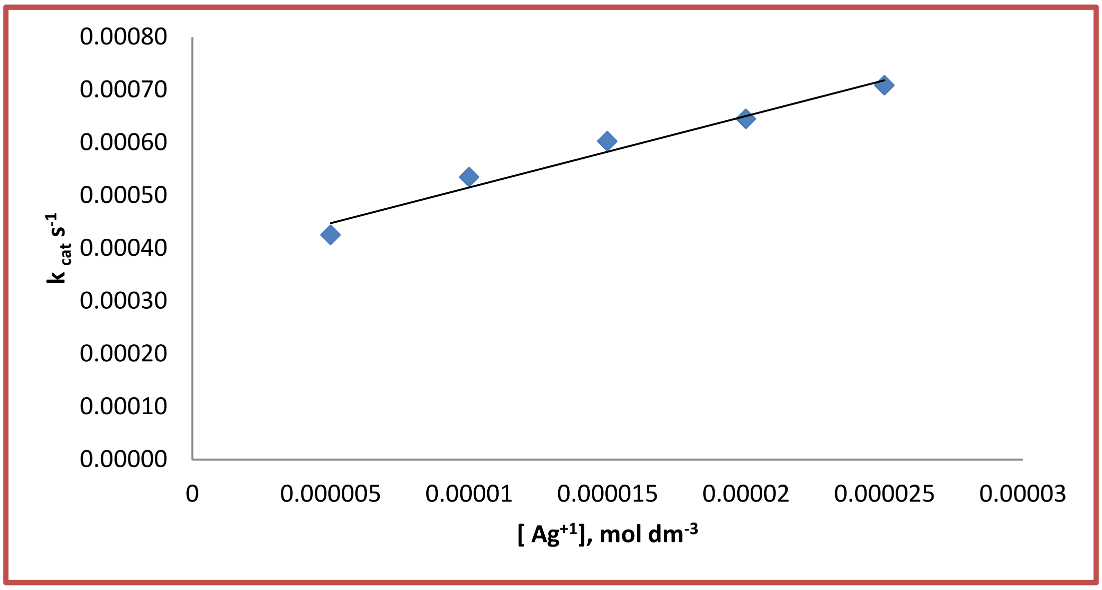
Variation of formic acid at [S(IV)]= $2x10^{-3}$ mol dm^{-3}, Ag (I) =$1x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	**$5x10^{-6}$**	**$8x10^{-6}$**	**$1x10^{-5}$**	**$3.5x10^{-5}$**	**$7.5x10^{-5}$**	**$1x10^{-4}$**	**$3x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.2	1.3	1.1	1.0	0.8	0.9	0.9
(10)	1.6	1.6	1.5	1.3	1.0	1.2	1.0
(15)	2.0	2.2	2.0	1.6	1.2	1.3	1.4
(20)	2.4	2.6	2.4	2.0	1.5	1.6	1.8
(25)	2.8	3.0	2.6	2.4	2.0	1.8	2.2
(30)	3.2	3.2	3.1	2.6	2.6	2.4	2.3
(40)	3.5	3.3	3.1	3.0	2.9	2.5	2.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**0.85**	**0.76**	**0.66**	**0.56**	**0.53**	**0.40**	**0.38**

Figures in parentheses denotes time in minute

[Formic acid] Dependence

To know the effect of formic acid on Ag (I) catalysed autoxidation of S(IV) formic acid variation was carried out from 5x10^{-6} mol dm^{-3} to 3 x 10^{-4} mol dm^{-3} at two different Ag (I) that is 5x10^{-6} mol dm^{-3} to 1 x 10^{-5} mol dm^{-3} but fixed S (IV) = 2x10^{-3} mol dm^{-3} at pH= 4.95 and t=30^{o} C. The results indicated that by increasing formic acid the rate becomes decelerates.



<u>Fig 3.4</u> : Effect of catalysts at [S(IV)] = 2x10^{-3} mol dm^{-3} , [Formic acid] =7.5x10^{-5} mol dm^{-3}, t= 30^{o} C, in acetate buffered medium. The value of intercept and slope are 3.7 x 10^{-4} s and1.3 x 10^{-1} mol dm^{-3} s respectively. Depending on the observed results the reaction follows the following rate law

$$-d\,[S(IV)]\,/dt \quad = \quad (k_1+k_2[Ag(I)]\,[S(IV)]\,/\,1 + B\,[Formic\ acid] \qquad (8)$$

Where k_{inh} = $(k_1+k_2[Ag(I)]\,/1 + B\,[Formic\ acid] = k_{cat}\,/\,1 + B\,[Formic\ acid]$ (9)

$$1/\ k_{inh} = 1 + B\,[Formic\ acid] \quad / \, k_{cat} \qquad (10)$$

$$1/\ k_{inh} = 1/\,k_{cat} + B\,[Formic\ acid]\,/\,k_{cat} \qquad (11)$$

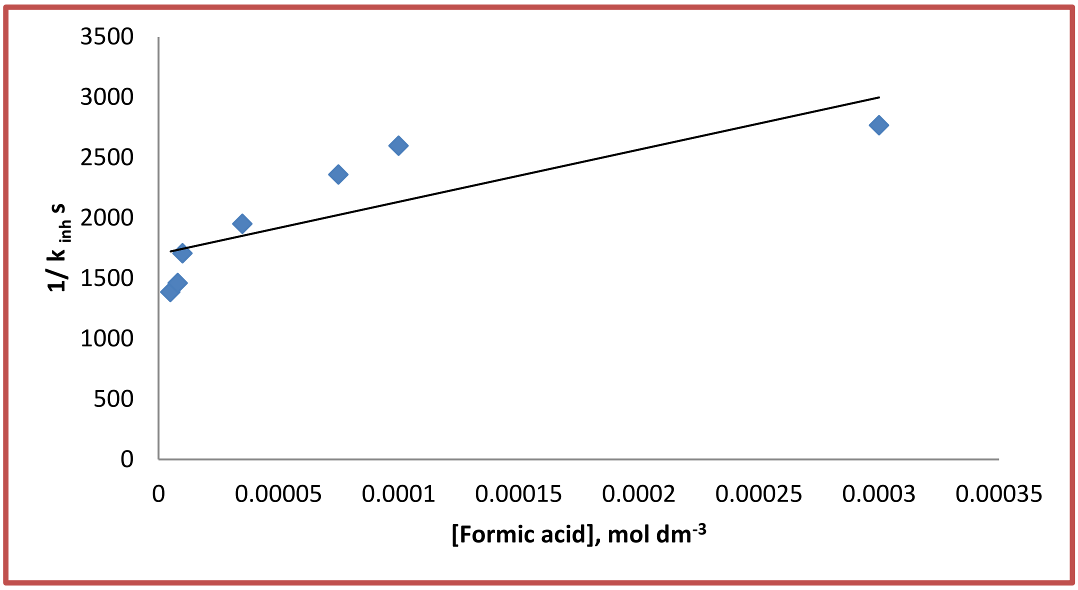


Fig 3.5 : Effect of formic acid at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^o C in acetate buffered medium. The Plot of $1/k_{inh}$ v/s [Formic acid] is linear with intercept 1.7 x 10^3 s and slope 4.32 x 10^6 mol dm^{-3} s from which the value of B = 2.53 x 10^3 mol dm^{-3}

Table - 3.30

The values of k_{inh} at different [Formic acid],[S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^o C CH_3COONa = $7x10^{-2}$ mol L^{-1} CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	$10^3 k_{inh}$ s^{-1}	$1/k_{inh}$ s
0.00	1.09	917
$5.0x10^{-6}$	0.72	1389
$8.0x10^{-6}$	0.69	1449
$1.0x10^{-5}$	0.59	1695
$3.5x10^{-5}$	0.51	1961
$7.5x10^{-5}$	0.42	2381
$1.0x10^{-4}$	0.38	2632
$3.0x10^{-4}$	0.36	2778

Effect of temperature

The values of k_{obs} were determined at three different temperatures in the range of 30^o C to 40^o C. The results are given in table 3.31. By plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 79.3 KJ mol^{-1}

Table–3.31

Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3} , Ag (I) = 5 $x10^{-6}$ mol dm^{-3} , [Formic acid] = 7.5 x 10^{-5} mol dm^{-3} ,

pH = 4.95

t ^{o} C	**10^3 k_{obs} S^{-1}**
30	0.42
35	0.62
40	0.74

Table - 3.32

Variation of [S(IV)] at Ag (I) =5x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10 ^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.5	0.6	1.2	2.7	3.9	4.6
(10)	0.7	0.8	2.0	3.9	5.2	6.6
(15)	0.9	1.5	2.9	4.8	6.6	8.8
(20)	1.1	2.0	3.5	5.9	7.7	9.5
(25)	1.2	2.4	4.7	6.7	9.2	11.7
(30)	1.4	2.7	5.5	8.7	11.6	14.3
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10 ^{3}) k_1 s^{-1}	**0.624**	**0.637**	**0.622**	**0.629**	**0.630**	**0.625**

Figures in parentheses denotes time in minutes

Table - 3.33

Variation of [S(IV)] at Ag (I) =5x10^{-6} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.4	0.7	1.2	2.5	4.5	5.6
(10)	0.7	0.9	2.2	4.2	6.5	7.8
(15)	1.2	1.6	3.2	5.5	8.2	10.2
(20)	1.5	2.2	4.5	7.7	10.2	12.5
(25)	1.5	2.9	6.3	8.8	12.5	14.7
(30)	1.7	3.4	6.6	10.2	13.6	17.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**1.06**	**1.00**	**1.01**	**1.00**	**1.01**	**1.02**

Figures in parentheses denotes time in minutes

Table - 3.34

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 35° C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.5	0.8	0.9	0.9
(10)	0.7	0.8	1.0	1.2	1.3
(15)	0.9	1.0	1.4	1.4	1.5
(20)	1.2	1.3	1.5	1.6	1.6
(25)	1.3	1.4	1.6	1.8	1.8
(30)	1.4	1.6	1.7	1.8	1.9
(40)	1.5	1.6	1.7	1.8	1.9
∞	2.0	2.0	2.0	2.0	2.0
(10^3) k_1 s^{-1}	**0.620**	**0.730**	**0.820**	**1.04**	**1.33**

Figures in parentheses denotes time in minutes

Table - 3.35

Variation of Ag (I) at S(IV)] = 2 x10^{-3} mol dm^{-3}, [Formic acid] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.5	0.8	0.9	0.9
(10)	0.7	0.8	1.0	1.2	1.3
(15)	0.9	1.0	1.2	1.4	1.5
(20)	1.2	1.3	1.5	1.6	1.6
(25)	1.4	1.4	1.6	1.7	1.8
(30)	1.4	1.6	1.6	1.8	1.9
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.740**	**0.860**	**0.920**	**1.21**	**1.54**

Figures in parentheses denotes time in minutes

Table - 3.36

Variation of formic acid at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 35^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	**$5x10^{-6}$**	**$8x10^{-6}$**	**$1x10^{-5}$**	**$3.5x10^{-5}$**	**$7.5x10^{-5}$**	**$1x10^{-4}$**	**$3x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.6	1.1	0.9	0.8	1.0	1.1	0.8
(10)	0.9	1.5	1.4	1.2	1.5	1.4	1.1
(15)	1.5	1.8	1.8	1.4	2	1.6	1.6
(20)	2.1	2.5	2.3	1.6	2.5	2.1	2.1
(25)	2.5	2.7	2.4	1.9	2.7	(30) 2.4	(30) 2.5
(30)	3.2	3.1	3.0	2.5	2.9	(50) 3.0	(50) 2.8
(40)				3.2			
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**0.828**	**0.785**	**0.703**	**0.603**	**0.537**	**0.434**	**0.408**

Figures in parentheses denotes time in minutes

Table - 3.37

Variation of formic acid at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) =5 $x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 40^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Formic acid] mol dm^{-3}	**$5x10^{-6}$**	**$8x10^{-6}$**	**$1x10^{-5}$**	**$3.5x10^{-5}$**	**$7.5x10^{-5}$**	**$1x10^{-4}$**	**$3x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.7	1.2	0.9	0.9	1.2	1.2	0.8
(10)	0.9	1.7	1.5	1.4	1.6	1.5	1.1
(15)	1.4	2.0	2	1.6	2.0	1.8	1.6
(20)	2.2	2.5	2.4	2.0	2.5	2.1	2.2
(25)	2.9	3.0	2.8	2.3	2.9	(30) 2.4	(30) 2.7
(30)	3.2	3.2	3.1	2.6	3.1	(50) 3.1	(50) 2.8
(40)				3.3			
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1s^{-1}	**0.901**	**0.871**	**0.812**	**0.660**	**0.615**	**0.455**	**0.422**

Figures in parentheses denotes time in minute

DISCUSSION

In aqueous solutions SO_2 is present in four forms $SO_2.H_2O, HSO_3^{-1}$, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH the following equilibrium operates :

$$HSO_3^{-1} \rightleftharpoons H^+ + SO_3^{-2} \qquad (12)$$

The equilibrium constant is 5.07x 10^{-7} In the experimental range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. During the course of reaction fraction order obtain is 0.20 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz (2008)[18] Bigelow et al (1898)[19] studied the effect of alcohols on the reactions between sodium sulphite and O_2 and found that the alcohols inhibited the reaction rate. Alyea et al (1929)[20] studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Backstrom (1934)[21] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2. Grgic et al (1998)[22] studied the inhibition effect of acetate, oxlate, format on Fe- catalysed autoxidation of S(IV) at pH 2.8, 3.7,4.5 and found that oxlate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe^{+3} due to formation of complexion with oxlate. Bostjan et al (2006)[23] studied the effect of carboxylic acid on Mn (II) catalysed oxidation of S (IV) and found that mono carboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag(I) catalysed reaction is decelerated by the addition of formic acid in the present study. Gupta et al (2008)[24] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3- 10^4 In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S (IV) by formic acid are found to be 3.33 x 10^4 mol dm^{-3} and 2.53 x 10 ^{3} mol dm^{-3} respectively. These values are in the same range as reported by Gupta et al. This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick and Zhang (1996)[25]

$$HSO_3^{-1} \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{-2} \quad K_d = 5.01 \times 10^{-7\,,\,26} \qquad (13)$$

$$Ag^+ + {}^-O_2CCH_3 \overset{K_{oAc}}{\rightleftharpoons} AgO_2CCH_3 \quad K_{oAc} = 2.29^{\,27} \qquad (14)$$

$$Ag^+ + SO_3^{-2} \overset{K_1}{\rightleftharpoons} AgOSO_2^- \quad K_1 = 2.51 \text{x } 10^{\,5,\,28} \qquad (15)$$

$$Ag^+ + HSO_3^{-1} \overset{K_2}{\rightleftharpoons} AgHSO_3 \qquad (16)$$

$$AgOSO_2^- + O_2 \overset{K_3}{\rightleftharpoons} AgOSO_2^{-1}.O_2 \qquad (17)$$

$$AgHSO_3 + O_2 \overset{K_4}{\rightleftharpoons} AgHSO_3.O_2 \qquad (18)$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (19)$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \qquad (20)$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \qquad (21)$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \qquad (22)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \qquad (23)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \qquad (24)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \qquad (25)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \qquad (26)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \qquad (27)$$

$$SO_4^{-\bullet} + \text{Formic acid} \xrightarrow{k_{10}} \text{Non Chain product} \qquad (28)$$

By assuming long chain hypothesis and steady state approximation $d[SO_3^{-\bullet}]/dt$, $d[SO_4^{-\bullet}]/dt$, $d[SO_5^{-\bullet}]/dt$, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 29)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Formic acid}]\}\ [SO_4^{-1}] \qquad (29)$$

Since the reaction is completely stopped in the presence of [Formic acid] at $8\text{x}10^{-4}$ mol dm^{-3}, so the step (22) and (25) appear to be unimportant. The step (24) is ignored because the reaction is completely seized in the presence of higher concentration of formic acid by omission and substitution from the above mechanism the following rate law can be obtain (30)

$R_{cat} = k_1 [Ag(I)] [S(IV)] / \{k_9[x] + k_{10} [\text{Formic acid}]\}$ (30)

Prasad et al (2013)[29] and Gupta et al (2008)[30] proposed a similar mechanism for the Co_2O_3 and CoO catalysed autoxidation of SO_2 inhibited by formic acid and ethanol respectively, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 2.53×10^3 mol dm^{-3} which is in the range of 10^3 - 10^4 and also coincide with the reported value of B of Co_2O_3 catalysed autoxidation of S(IV) by formic acid is 3.58×10^{3} mol dm^{-3} So on the basis of calculated value of B we concluded that formic acid act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

CONCLUSIONS

The following conclusions are deduced from the results of the formic acid inhibited Ag (I) catalysed autoxidation of S(IV) was that inhibit the oxidation with the moderate influence. The value of Inhibition factor of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are in the range of 10^3 -10^4 which shows that free radical mechanism is operative.

REFERENCES

1. Calvert J.G., Heikes B.G., Stock well W.R., Mohen V.A. and Kerr J. A., 1986, "Some considerations of the important chemical process in acid deposition in chemistry of multiphasic atmospheric systems" springer Verlog Heidelberg, pp 615-647.
2. Berreshim W. and Jaeshke W.,1986, 'Study of metal aerosol systems such as sink for atmospheric SO_2, *J Atmoschem,* **4**, 311-344.
3. Grosjean D., 1982, Formaldehyde and other carbonyls in Los Angeles ambient air, *Environmental Science and Technology,* **16**, 254–262.
4. Grosjean D., Wright B., 1983, Carbonyls in urban fog, ice fog, cloud-water and rainwater, *Atmospheric Environment*, **17**, 2093–2096.
5. Kawamura K., Ng L.L., Kaplan I.R., 1985a, Determination of organic acids (C1–C10) in the atmosphere, motor exhausts and engine oils, *Environmental Science and Technology,* **21**,105–110.
6. Kawamura K., Steinberg S., Kaplan I.R., 2000, Homologous series of C1–C10 mono carboxylic acids and C1–C6 carbonylsin Los Angeles air and motor vehicle exhausts, *Atmospheric Environment*, **34**, 4175–4191.
7. Keene W.C., Galloway J.N., Holden Jr. J.D., 1983, Measurement of weak organic acidity in precipitation from remote areas of the world. *Journal of Geophysical Research,* **88**, 5122–5130.
8. Khwaja H.A., 1995, Atmospheric concentrations of carboxylic acids and related compounds at a semi urban site. *Atmospheric Environment,* **29**, 127-139.
9. Talbot R.W., Andreae M.O., Berresheim, H., Jacob D.J., Beecher K.M., 1990, Source and sink of formic and acetic, and pyruvic acids over central Amazon, *Journal of Geophysical Research, 95*, 16799–16811.
10. Talbot R.W., Beecher K.M., Harriss R.C., Coter III, W.R., 1988, Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site, *Journal of Geophysical Research,* **93**, 1638–1652.

11. Helas G., Bingomer H., Andreal M.O., 1992, Organic acids over equatorial Africa, result from DECAFE 88, *Journal of Geophysical Research*, **97**, 6187–6193.
12. Kawamura K., Kasukabe H., Barrie L.A., 1996a, Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in Arctic aerosols, one year of observations, *Atmospheric Environment*, **30**, 1709–1722.
13. Kawamura K., Steinberg S., Kaplan I.R., 1985b, Capillary GC determination of short-chain dicarboxylic acids in rain, fog and mist. *International Journal of Environmental Analytical Chemistry,* **19**, 175–188.
14. Chebbi A., Carlier P., 1996, Carboxylic acids in the troposphere, occurrence, sources, and sinks, a review, *Atmospheric Environment,* **30**, 4233–4249.
15. Gupta K. S., Bhargava P., Manoj S. V. and Bhargava R., 2000, Kinetics and mechanism of silver(I) catalyzed oxidation of aqueous sulfur(IV) in acetate buffered medium. *Transition Metal Chemistry***,** **25**, 329-332
16. Martin L. R., 1984, In *SO_2, NO and NO_2 Oxidation Mechanisms, Atmospheric Considerations*, Calvert, J. G. (Ed.), Butterworth, Boston**.** pp 63-100.
17. Kawamura K., Steinberg S., Kaplan I.R., 2000, Homologousseries of C1–C10 mono carboxylic acids and C1-C6 carbonyls in Los Angeles air and motor vehicle exhausts, *Atmospheric Environment,* **34**, 4175–4191.
18. Irena Wilkosz, Maninka Anna, 2008, Mn (II) catalysed S (IV) oxidation and its inhibition by acetic acid in acidic aqueous solutions, *J atmos Chem.* **60**, 1-17.
19. Bigelow S. L., 1988, Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.
20. Alyea H. N. and Backstrom, H. L. J., 1929, The inhibitive action of alcohols on the autoxidation of sodium sulfite*, Journal of American Chemical Society,* **51**, 90-107**.**

21. Backstrom H. L. J., 1934, The chain mechanism of the autoxidation of sodium sulfite solutions, *J. Phys. Chem.*(B), **25**, 122-138.
22. Grgic I., Dovzan A., Bercic G., and Hudnik V., 1998, The effect of atmospheric organic compound son the Fe-catalyzed S(IV) autoxidation in aqueous solution, *J. Atmos. Chem.*, **29**, 315–337.
23. Podkrajsek B., Grgic I. and Tursic J., 2006, Influence of atmospheric carboxylic acid on catalytic oxidation of S(IV), *J of atmospheric chemistry*, **54**, 103-120.
24. Yogpal Dayal, K.S. Gupta, 2014, The influence of hydroxyl organic compounds on the oxidation of SO_2 by oxygen, *Env. Sc. Pollu Res*, Vol **21**, 7808-7817.
25. R.E. Connick, Y.X. Zhang, S. Lee, R. Adamic and P. Cheing, 1995, Kinetics and mechanism of oxidation of HSO_3^- by O_2 the uncatalysed reactions, *Inorg. Chem.*, **34**, 4543.
26. L.G. Sillen and A.E. Martell, 1964, stability constants of metal ion complex special publication no 17, The chemical soc. Burlington house London.
27. V.F. Toropova I.A. Sirotina and V.B. Rotanova, 1955, Uchenye Zapiski Kazanskogo Uni. 115, no. 353.
28. R. Van Eldik and G.M. Harris, 1980, *Inorg Chem.*, **19**, 880.
29. Sameena Begam, Faiyaz Huusain, D.S.N. Prasad, 2013, Kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Pelagia Research Library*, **4(1)**, 122-131.
30. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., 2008, Kinetics of the uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 Catalyzed autoxidation of Sulfur (IV) in alkaline medium, *Transition Metal Chemistry*, **33**, 809-817.

CHAPTER - IV

Kinetics of Isopropyl Alcohol Inhibited Uncatalysed and Ag (I) Catalysed Autoxidation of S (IV) in Acidic Medium

ABSTRACT

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. Based on the observed results a free radical mechanism operative and following rate law has been proposed.

$-d\,[S(IV)/dt \;=\; (k_1+k_2[Ag])\,[S(IV)]/\,1 + B\,[\text{Isopropyl alcohol}]$

INTRODUCTION

Alcohols commonly present both in urban and in rural atmosphere add to the group of pollutants termed volatile organic compounds (VOCs) reported by (J. Ziajka, W. Pasiuk-Bronikowska 2003)[17]. The gas-phase concentration of ethanol may be even as high as 226 ppbv; whereas the maximum concentration determined, for instance, for phenol is only 2.5 ppbv (Isidorov, 2001)[16]. The aqueous-phase concentration of methanol and ethanol assumed as representative for urban atmosphere conditions is 1.8×10^{-6} M and 3.1×10^{-7} M respectively (Herrmann et al., 2000)[14]. The interaction between alcohols and the SO_2 oxidation intermediates may have a bearing on acidity formation in the atmosphere. Bigelow (1898)[4] was the first who found experimentally that alcohols, such as methanol, ethanol, propanol and butanol, slow down the reaction between sodium sulphite and air oxygen. His aim was to gain some quantitative data to widen the knowledge on catalysis. The inhibiting effect of aliphatic alcohols (ethanol, isopropanol, secondary butanol and benzyl alcohol) on the oxidation of sodium sulphite was then investigated by Alyea and Backstrom (1929)[1] in a chain reaction theory-based study. These authors gave the following rate expression:

$$R_d = k_1/(kC+k_2) \qquad (1)$$

The experiments described by the above equation were performed under alkaline conditions (Initial pH 8.4). Later, Backstrom (1934)[3] developed the radical mechanism of the reaction between sodium sulphite and oxygen to show the probable contribution of such radicals as $SO_3^{-\bullet}$, $SO_4^{-\bullet}$ and $SO_5^{-\bullet}$ in the formation of a chain and to explain the previously observed alcohol inhibition by the reaction:

$$RCH_2OH + SO_5^{-\bullet} \longrightarrow RCHO + SO_4^{-\bullet} + H_2O \qquad (2)$$

The interests of further researchers were focused on gaining the direct experimental evidence for the reactivity of sulphoxy radicals with respect to alcohols which resulted in proving the unshakable ability of these compounds to react with $SO_4^{-\bullet}$ (Ashmore 1963[2] , Gilbertet al. 1988[9], Dogliotti and Hayon 1967[8], Clifton and Huie 1989[5]), whereas reactions with $SO_3^{-\bullet}$ and $SO_5^{-\bullet}$ occurred unimportant (Hayon et al., 1972)[13] A strong impulse to develop experimental studies on the kinetics and products of sulphate radical–alcohol reactions was when it occurred clear that these reactions may be of importance in chemistry of atmospheric aqueous phase (Clifton and Huie 1989[5], Wine et al. 1989[25], Warneck et al. 1994[24], Ziajka et al., 2001[27] Ziajka and Pasiuk- Bronikowska, 1999[28], 2000[29], 2003[30]). The methanol inhibition of the uncatalysed autoxidation of HSO_3 was investigated by (Connick et al.1995[7]) to shed more light on a mechanism of initiation in the absence of transition metal ions (Connick and Zhang 1996[6]), showed that in the presence of manganous ions the inhibition by methanol is more complex than indicated by simply adding to the overall reaction mechanism the step by which sulphate radicals are scavenged. Since it is planned to study the kinetics of Ag (I) catalysed oxidation of S(IV) by O_2 in acidic medium in the presence of Isopropyl alcohol to examine its effect on the reaction rate.

EXPERIMENTAL

The experimental procedure was exactly the same as described earlier[29]. All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature $30 \pm 1\ ^{0}C$. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at 1600 ± 10 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreached S(IV) iodometrically. The reproducibility of replicate measurements was generally better than 10$\underline{+}$1 %. All calculations were performed in MS Excel.

PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S(VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure.

The product analysis showed the recovery of sulphate to be 98$\underline{+}$1%., in all cases in agreement with eq. (3)

$$S(IV) + 0.5\ O_2 \xrightarrow{\qquad} S\ (VI) \qquad (3)$$

RESULTS

Preliminary Investigation

The kinetics of both uncatalysed and Ag (I) catalysed and isopropyl alcohol inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30^o C. In both the cases the first order dependence of S (IV) was observed in the kinetics data treatment for the determination of first order rate constant k_1 was carried out from log [S(IV)] versus time, t. The plots were shown in fig 4.1. From the fig.4.1 observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by isopropyl alcohol.

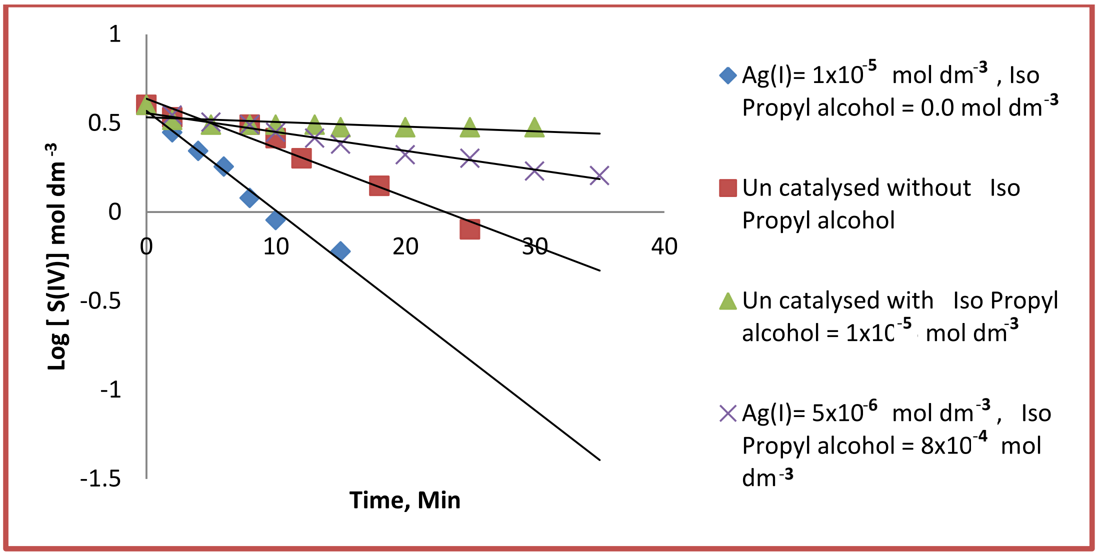


Fig. 4.1 :The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2x 10^{-3} mol dm^{-3} at pH = 4.95, t = 30^{o} C

(◇) Ag (I) = 1x 10^{-5}mol dm^{-3}, [Isopropyl alcohol] = 0.0 mol dm^{-3}

(□) Uncatalysed without isopropyl alcohol

(△) Uncatalysed with [Isopropyl alcohol] = 1x10^{-5} mol dm^{-3}

(x) Ag (I) = 5x 10^{-6}mol dm^{-3}, [Isopropyl alcohol] = 8x 10^{-4} mol dm^{-3}

Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of Ag (I) and all the solutions were prepared in doubly distilled water.

Table- 4.1

Quantitative Analysis of Sulphate in Final Product Solution

10^3 [S(IV)] mol dm^{-3}	**Ag (I) mol dm^{-3}**	**pH**	**10^3 [SO_4^{-2}] mol dm^{-3}**	**[SO_4^{-2}] /[S(IV)]**	**% of S(IV) recovery**
5.0	0.00	4.95	4.90	0.980	98.0
5.0	$5x10^{-6}$	4.95	4.92	0.984	98.4
5.0	$1x10^{-5}$	4.95	4.95	0.990	99.0

Table- 4.2

Variation of [S (IV)] at pH = 4.95, t = 30° C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**3**	**4**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot			
(0)	0.0	0.0	0.0	0.0
(2)	0.5	0.6	1.3	1.6
(8)	0.8	0.9	2.1	2.2
(10)	1.0	1.4	3.2	3.2
(12)	1.2	2.0	3.8	4.3
(18)	1.4	2.6	4.6	5.4
(25)	1.6	3.2	4.8	6.5
∞	2.0	4.0	6.0	8.0
(10^3) k_1 s^{-1}	**1.04**	**1.06**	**1.09**	**1.09**

Figures in parentheses denotes time in minutes

Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range 1x10^{-3} mol dm^{-3} to 4x10^{-3} mol dm^{-3} at pH = 4.95, t=30^{o} C in acetate buffered medium. The kinetics was found to be first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of first order rate constant k_1 are given in table-4.3. The dependence of reaction rate on [S(IV)] follows the rate law (4)

$$-d [S(IV)] /dt = k_1 [S(IV)] \qquad (4)$$

Table- 4.3

The Values of k_1 for uncatalysed reaction at different [S(IV)] at pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

[S(IV)] mol dm^{-3}	(10^3) k_1 s^{-1}
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

[Isopropyl alcohol] Dependence

The major aim of this study was to examine the effect of isopropyl alcohol on the autoxidation of S(IV) in acetate buffer medium and varying the [Isopropyl alcohol] from 5x10^{-7} mol dm^{-3} to 8x10^{-4} mol dm^{-3}, we observed the rate of the reaction decreased by increasing [Isopropyl alcohol]. The results are given in table 4.4. However the nature of the [S(IV)] dependence in presence of isopropyl alcohol did not change and remains first order. The first order rate constant k_{inh}, in the presence of isopropyl alcohol was defined by rate law (5)

$$-d\,[S(IV)]/dt = k_{inh}\,[S(IV)] \qquad (5)$$

The values of k_{inh} in the presence of isopropyl alcohol decreased with increasing [Isopropyl alcohol] are given in table 4.5 which are in agreement with the rate law (6)

$$k_{inh} = k_1 / (1+B\,[\text{Isopropyl alcohol}] \qquad (6)$$

Where B is inhibition parameter for rate inhibition by Isopropyl alcohol

The equation (6) on rearrangement becomes

$$1/k_{inh} = 1/k_1 + B\,[\text{Isopropyl alcohol}] / k_1 \qquad (7)$$

In accordance with the equation (7) the plot of $1/k_{inh}$ v/s [Isopropyl alcohol] was found to be linear with non- zero intercept fig 4.2 The values of intercept ($1/k_1$) and slope (B/k_1) were found to be 1.11×10^4 s and 5.47×10^6 mol dm^{-3} s at pH = 4.95, t = 30^o C. From these values the value of inhibition parameter B was found to be 4.92×10^3 mol dm^{-3}

Table- 4.4

Variation of [Isopropyl alcohol], at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-7}$**	**$3x10^{-6}$**	**$5x10^{-6}$**	**$1 x10^{-5}$**	**$5x10^{-5}$**	**$7x10^{-5}$**	**$3x10^{-4}$**	**$8x10^{-4}$**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.6	0.7	0.8	0.6	0.7	0.5	0.3	0.3
(5)	0.9	0.8	1.0	1.2	0.9	1.0	0.8	0.5	0.5
(8)	1.2	1.3	1.3	1.5	1.2	1.3	1.0	0.8	0.6
(10)	1.9	1.5	1.6	1.9	1.5	1.5	1.3	1.0	0.7
(13)	2.2	1.8	1.9	2.2	1.8	1.9	1.5	1.3	0.8
(15)	2.6	2.5	2.5	2.5	2.2	2.4	1.8	1.5	0.9
(20)	3.3	3.2	3.0	2.9	2.4	2.6	2	1.8	1.0
(25)	3.3	3.2	3.2	3.0	2.8	2.8	2.2	1.8	1.1
(30)	3.4	3.4	3.4	3.3	3.1	3.0	2.3	1.9	1.2
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.17**	**1.13**	**1.08**	**0.93**	**0.80**	**0.77**	**0.48**	**0.38**	**0.18**

Figures in parentheses denotes time in minute

Table- 4.5

The values of k_{inh} at different [Isopropyl alcohol] pH = 4.95, t = 30° C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	**10^3 k_{inh} s^{-1}**	**$1/k_{inh}$ s**
$5.0x10^{-7}$	1.17	855
$8.0x10^{-7}$	1.1.3	885
$3.0x10^{-6}$	1.08	926
$5.0x10^{-6}$	0.93	1075
$1.0x10^{-5}$	0.80	1250
$5.0x10^{-5}$	0.77	1299
$7.0x10^{-5}$	0.48	2083
$3.0x10^{-4}$	0.38	2632
$8.0x10^{-4}$	0.18	5556

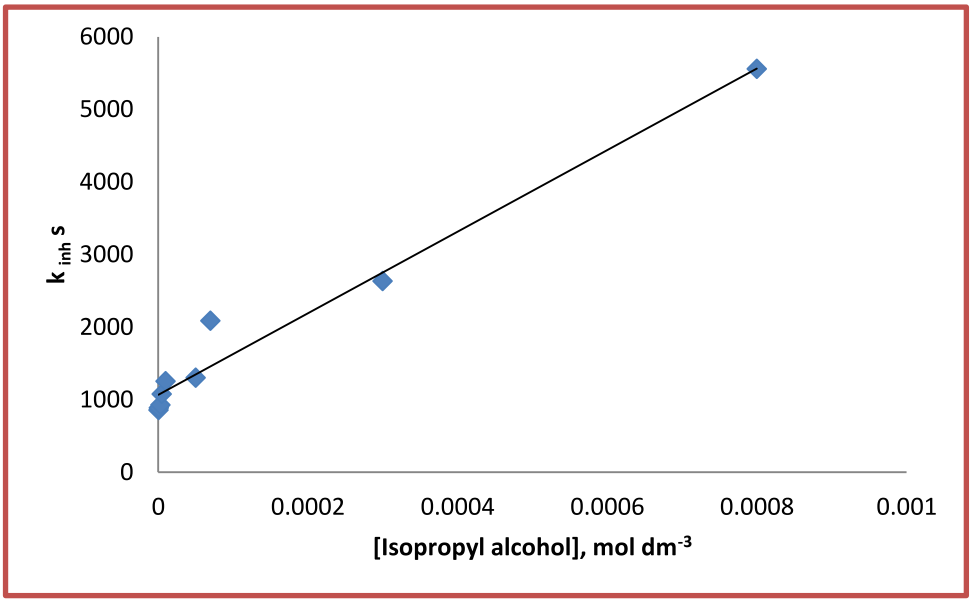


Fig 4.2 : Effect of Isopropyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30° C in acetate buffered medium

Ag(I) Catalysed Reaction

At first the kinetics of Ag(I) Catalysed reaction in the absence of inhibitor was studied.

[S(IV)] Variation

The dependence of S (IV) on reaction rate was studied by varying [S(IV)] from $1x10^{-3}$ mol dm^{-3} to $10x10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5x10^{6}$ mol dm^{-3} and $1x10^{-5}$ mol dm^{-3} at pH = 4.95, t = 30^{o} C. The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in fig 4.1

Ag(I) Variations

The dependence of Ag(I) on the reaction rate was studied by varying Ag(I) from $5x10^{-6}$ mol dm^{-3} to $2.5x10^{-5}$ mol dm^{-3} at S(IV) = $2x10^{-3}$ mol dm^{-3} pH= 4.95, t = 30^{o} C in acetate buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig 4.3. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law – (8)

$$-d\,[S(IV)]\,/dt \quad = k_{cat}\,[S(IV)] \;= (k_1+k_2[Ag(I)]\,[S(IV)] \qquad (8)$$

$$\text{Or} \qquad k_{cat} \qquad = \quad k_1+k[Ag(I)] \qquad (9)$$

From the plot in fig 4.3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be 0.72x $10^{\ 1}$ s and 8.6 x 10^{-3} mol dm^{-3} respectively at pH = 4.95, t = 30^{o} C, in acetate buffered medium.

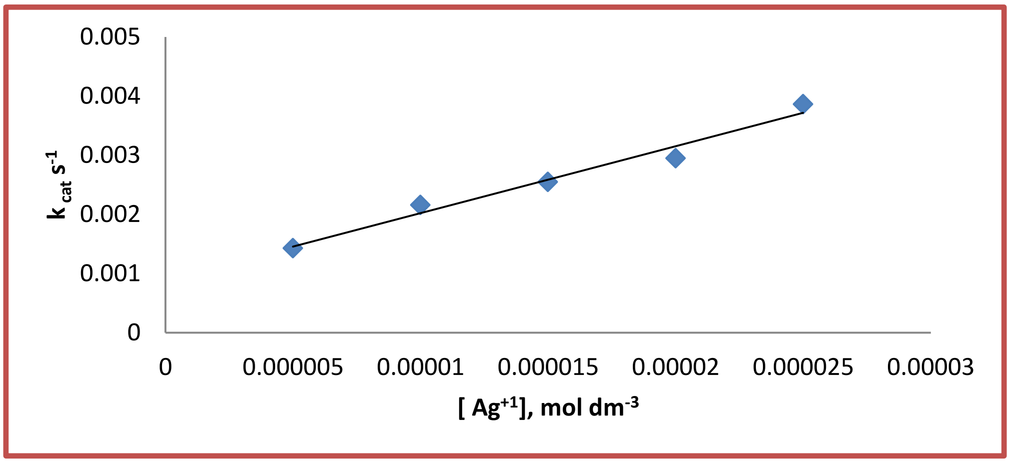


Fig 4.2 : The dependence of catalyst concentration at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium

Table- 4.6

Variation of [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3} at Ag (I) =$5\text{x}10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}, CH_3COOH = $3\text{x}10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.8	1.5	2.0	2.2
(4)	0.4	1.0	1.7	2.4	3.3	4.5
(6)	0.6	1.2	2.7	3.0	4.5	6.5
(8)	0.9	1.5	3.6	4.0	7.0	9.8
(10)	1.2	1.7	5.0	5.5	9.3	12.1
(15)	1.4	3.0	5.5	9.0	11.5	14.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.43**	**1.42**	**1.41**	**1.44**	**1.46**	**1.50**

Figures in parentheses denotes time in minutes

Table- 4.7

Variation of [S(IV)] = 2×10^{-3} mol dm^{-3} at Ag (I) =1×10^{-5} mol dm^{-3} pH = 4.95, t = 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH = 3×10^{-2} mol L^{-1}

10 ^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10 $^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.9	3.0	4.5	5.6
(4)	0.8	1.8	2.8	4.8	6.3	7.8
(6)	1.2	2.2	3.6	5.9	7.8	9.5
(8)	1.4	2.8	4.5	7.8	8.9	10.2
(10)	1.5	3.1	5.0	8.9	12.5	12.8
(15)	1.7	3.4	7.0	10.3	13.6	17.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**2.19**	**2.15**	**2.15**	**2.18**	**2.14**	**2.10**

Figures in parentheses denotes time in minutes

Table- 4.8

Variation of Ag (I) at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}, CH_3COOH = $3\text{x}10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5\text{x}10^{-6}$**	**$1\text{x}10^{-5}$**	**$1.5\text{x}10^{-5}$**	**$2\text{x}10^{-5}$**	**$2.5\text{x}10^{-5}$**
Time, (Min)	Volume of 5 x10^{-3}mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.4	2.5	2.4
(4)	1.0	1.8	1.8	2.7	2.5
(6)	1.2	2.2	2.0	2.9	3.0
(8)	1.5	2.8	2.2	3.7	3.5
(10)	1.7	3.1	3.4		
(15)	3.0	3.4			
∞	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.42**	**2.15**	**2.54**	**2.94**	**3.88**

Figures in parentheses denotes time in minutes

Table - 4.9

The values of k_{cat} at different concentration of Ag (I) mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	10 ^{3} k_{cat} s^{-1}
0.000005	1.42
0.00001	2.15
0.00015	2.54
0.00020	2.94
0.00025	3.88

Variation of pH

Variation of pH was carried out from 4.02-5.25 at different [S(IV), Ag (I), [Isopropyl alcohol] and temperatures. The rate decreases slightly by varying pH is inverse H^{+} ion dependence was observed. From the plot of log k_1 v/s log (H^{+}) the order with respect to H^{+} is 0.30 which is a fractional order and can be neglected as shown in fig 4.4

Table - 4.10

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3} [Isopropyl alcohol] =7.0x10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa=7x10^{-2} mol L^{-1}

pH	10 ^{3} ks^{-1}
4.02	0.401
4.35	0.523
4.56	0.611
4.75	0.726
4.95	0.859
5.25	0.925

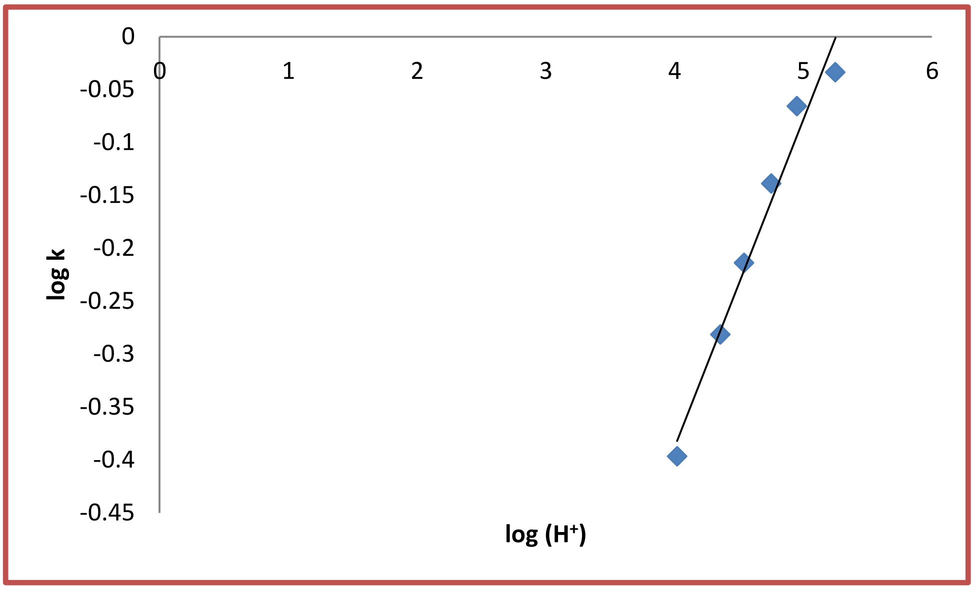


Fig.4.4 : Effect of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Isopropyl alcohol]= 7.0x10^{-5} mol dm^{-3}, t= 30^{o} C in acetate buffered medium.

Table - 4.11

Rate of Ag (I) catalysed autoxidation in the presence of isopropyl alcohol.

[Isopropyl alcohol], mol dm^{-3}	Ag (I) = 5x10^{-6} mol dm^{-3}	Ag (I) =1x10^{5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.02			
7.0 x 10^{-5}	0.401 x 10^{-3}	0.569 x 10^{-3}	0.670 x 10^{-3}
3.0 x 10^{-4}	0.264 x 10^{-3}	_	_
8.0 x 10^{-4}	0.170 x 10^{-3}	_	_
pH = 4.50			
7.0 x 10^{-5}	0.611 x 10^{-3}	0.722 x 10^{-3}	0.860 x 10^{-3}
3.0 x 10^{-4}	0.407 x 10^{-3}	_	_
8.0 x 10^{-4}	0.337 x 10^{-3}	_	_
pH = 5.25			
7.0 x 10^{-5}	0.925 x 10^{-3}	1.16 x 10^{-3}	1.46 x 10^{-3}
3.0 x 10^{-4}	0.582 x 10^{-3}	_	_
8.0 x 10^{-4}	0.430 x 10^{-3}	_	_

Table - 4.12

Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of isopropyl alcohol.

[Isopropyl alcohol] 7.0×10^{-5} mol dm^{-3}	**Ag (I) =$5x10^{-6}$ mol dm^{-3}**	**Ag (I) = $1x10^{5}$ mol dm^{-3}**	**Ag (I) = $1.5x10^{5}$ mol dm^{-3}**
pH = 4.50			
	2.49	2.97	2.18

Table - 4.13

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isopropyl alcohol] = $7x10^{-5}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.6	0.7	1.2	0.5	0.5
(5)	0.8	0.9	0.9	1.5	0.8	0.8
(8)	1.0	1.1	1.1	1.9	1.2	1.1
(10)	1.2	1.3	1.4	2.2	1.5	1.5
(13)	1.4	1.5	1.6	2.4	1.7	1.8
(15)	1.6	1.8	2.0	2.9	2.2	2.2
(20)	1.8	2.0	2.2	3.0	2.5	2.4
(25)	2.1	2.2	2.4	3.0	2.9	2.9
(30)	2.2	2.5	2.7	3.1	3.0	3.3
(35)	2.3	2.8	3.0	3.2	3.4	3.4
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.401**	**0.523**	**0.611**	**0.726**	**0.859**	**0.925**

Figures in parentheses denotes time in minutes

Table -4.14

Variation of pH at [S(IV)] = 4×10^{-3} mol dm^{-3}, Ag (I) = 5×10^{-6} mol dm^{-3}, [Isopropyl alcohol] = 7×10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2}mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.1	1.2	1.3	1.5	1.5	1.5
(5)	1.5	1.5	1.9	2.0	2.0	2.2
(8)	2.0	2.1	2.2	2.5	2.5	2.6
(10)	2.3	2.5	2.6	2.9	2.9	3.0
(13)	2.7	3.0	3.1	3.4	3.4	3.5
(15)	3.2	3.4	3.7	4.2	4.2	4.2
(20)	3.6	3.8	4.2	5.1	5.1	5.1
(25)	4.2	4.3	4.9	6.0	6.0	6.1
(30)	4.3	5.1	5.3	6.0	6.2	6.4
(35)	4.7	5.5	6.0	6.0	6.5	6.9
∞	8.0	8.0	8.0	8.0	8.0	8.0
(10^3) k_1, s^{-1}	**0.404**	**0.510**	**0.607**	**0.722**	**0.816**	**0.916**

Figures in parentheses denotes time in minutes

Table 4.15

Variation of pH at [S(IV)] = 6x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, t= 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	2.2	2.3	2.5	2.6	2.8	2.8
(5)	2.8	3.0	3.4	3.5	3.6	3.6
(8)	3.4	3.5	4.2	4.4	4.5	4.5
(10)	4.1	4.3	5.2	5.5	5.6	5.6
(13)	4.6	4.9	6.5	6.6	6.9	6.9
(15)	5.1	5.5	7.1	7.3	7.4	7.4
(20)	5.9	6.2	8.2	8.4	8.8	8.8
(25)	6.2	7.0	8.5	8.9	9.0	9.4
(30)	6.4	7.5	8.8	9.2	9.3	9.9
(35)	7.5	8.5	8.9	9.2	10.0	10.3
∞	12.0	12.0	12.0	12.0	12.0	12.0
(10^3) k_1, s^{-1}	**0.403**	**0.524**	**0.664**	**0.726**	**0.823**	**0.930**

Figures in parentheses denotes time in minutes

Table - 4.16

Variation of pH at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = $1\text{x}10^{-5}$ mol dm^{-3}, [Isopropyl alcohol] = $7\text{x}10^{-5}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	0.9	0.9	1.0	1.2
(5)	0.9	1.0	1.3	1.4	1.5	1.5
(8)	1.2	1.3	1.6	1.8	1.9	2.0
(10)	1.5	1.6	1.9	2.0	2.3	2.4
(13)	1.8	1.9	2.4	2.4	2.5	2.9
(15)	2.1	2.2	2.8	2.8	2.9	3.3
(20)	2.3	2.4	3.0	3.1	3.3	3.4
(25)	2.4	2.6	3.0	3.2	3.3	3.5
(30)	2.6	2.8	3.0	3.3	3.4	3.6
(35)	2.9	2.9	3.1	3.3	3.5	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.569**	**0.604**	**0.722**	**0.875**	**0.998**	**1.160**

Figures in parentheses denotes time in minutes

Table -4.17

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $1.5x10^{-5}$ mol dm^{-3}, [Isopropyl alcohol] = $7x10^{-5}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	0.9	1.0	1.0	1.2
(5)	1.1	1.2	1.2	1.2	1.4	1.5
(8)	1.4	1.6	1.6	1.6	1.6	1.8
(10)	1.6	1.8	2.0	2.1	2.3	2.4
(13)	1.8	2.0	2.3	2.4	2.6	2.7
(15)	2.2	2.3	2.5	2.8	2.8	3.0
(20)	2.4	2.8	3.0	3.0	3.2	3.2
(25)	2.6	3.0	3.2	3.2	3.3	3.5
(30)	2.9	3.1	3.2	3.3	3.6	3.5
(35)	3.1	3.1	3.3	3.4	3.6	3.9
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.670**	**0.747**	**0.860**	**0.915**	**1.15**	**1.460**

Figures in parentheses denotes time in minutes

Table - 4.18

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5×10^{-6} mol dm^{-3}, [Isopropyl alcohol] = 3×10^{-4} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	4.02	4.35	4.56	4.75	4.95	5.25
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.6	0.6	0.8	0.7	0.5
(5)	0.6	0.8	0.9	0.9	1.0	0.8
(8)	0.8	1.0	1.1	1.2	1.3	1.1
(10)	1.0	1.2	1.4	1.5	1.5	1.4
(13)	1.2	1.3	1.5	1.6	1.7	1.6
(15)	1.3	1.5	1.7	1.9	2.0	1.8
(20)	1.4	1.6	1.9	2.0	2.3	2.0
(25)	1.5	1.8	2.0	2.2	2.5	2.3
(30)	1.6	2.0	2.3	2.4	2.6	2.5
(35)	1.9	2.2	2.4	2.5	2.8	3.0
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1,s^{-1}	**0.264**	**0.337**	**0.407**	**0.435**	**0.549**	**0.582**

Figures in parentheses denotes time in minutes

Table 4.19

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3} Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isopropyl alcohol] = $8x10^{-4}$ mol dm^{-3}, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.4	0.5	0.7	0.5	0.4
(5)	0.5	0.5	0.7	0.9	0.8	0.6
(8)	0.6	0.7	0.9	1.0	0.9	0.9
(10)	0.7	0.9	1.0	1.2	1.2	1.0
(13)	0.9	1.0	1.2	1.4	1.4	1.2
(15)	1.0	1.2	1.3	1.6	1.6	1.3
(20)	1.1	1.3	1.5	1.8	1.9	1.4
(25)	1.2	1.4	1.8	2.0	2.0	1.8
(30)	1.2	1.5	2.0	2.1	2.3	2.1
(35)	1.3	1.6	2.1	2.2	2.4	2.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.170**	**0.229**	**0.337**	**0.356**	**0.426**	**0.430**

Figures in parentheses denotes time in minutes

Table - 4.20

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5×10^{-6} mol dm^{-3}, [Isopropyl alcohol] = 7×10^{-5} mol dm^{-3}, t= 35^o C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.7	0.8	0.8	0.9	0.9
(5)	0.8	0.9	1.0	1.2	1.2	1.3
(8)	1.0	1.1	1.2	1.5	1.5	1.5
(10)	1.2	1.4	1.5	1.7	1.7	1.8
(13)	1.5	1.6	1.7	2.0	2.1	2.2
(15)	1.7	1.8	2.0	2.3	2.5	2.5
(20)	2.0	2.0	2.3	2.5	2.8	2.8
(25)	2.3	2.4	2.5	2.9	3.0	3.1
(30)	2.6	2.6	2.6	3.1	3.2	3.3
(35)	2.7	2.9	3.2	3.2	3.4	3.5
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.532**	**0.565**	**0.650**	**0.757**	**0.873**	**0.950**

Figures in parentheses denotes time in minutes

Table 4.21

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5×10^{-6} mol dm^{-3}, [Isopropyl alcohol] = 7×10^{-5} mol dm^{-3}, t= 40^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.9	0.8	0.9	1.0	1.0
(5)	1.0	1.2	1.2	1.3	1.3	1.4
(8)	1.3	1.4	1.4	1.6	1.6	1.6
(10)	1.5	1.7	1.6	2.0	1.9	1.9
(13)	1.9	2.0	2.2	2.3	2.2	2.3
(15)	2.0	2.3	2.5	2.5	2.6	2.5
(20)	2.3	2.5	2.7	2.7	2.9	3
(25)	2.5	2.7	3.0	3.0	3.1	3.3
(30)	2.7	2.9	3.1	3.2	3.3	3.5
(35)	2.9	3.0	3.2	3.4	3.5	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.578**	**0.638**	**0.782**	**0.849**	**0.944**	**1.09**

Figures in parentheses denotes time in minutes

Table- 4.22

Variation of [S(IV)] at Ag (I) = 5 x10^{-6} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.5	1.5	2.8	3.2	3.2
(5)	0.0	0.8	2.0	3.6	5.5	5.2
(8)	0.1	1.2	2.5	4.5	6.2	7.3
(10)	0.1	1.5	2.9	5.6	7.4	8.8
(13)	0.1	1.7	3.4	6.9	8.5	10.4
(15)	0.1	2.2	4.2	7.4	9.2	12.2
(20)	0.2	2.5	5.1	8.8	10.5	14.4
(25)	0.2	2.9	6.0	9.0	11.4	15.4
(30)	0.2	3.0	6.2	9.3	13.2	16.5
(35)	0.4	3.4	6.5	10.0	13.8	16.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.888**	**0.859**	**0.816**	**0.823**	**0.885**	**0.895**

Figures in parentheses denotes time in minutes

Table- 4.23

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$mol dm^{-3} [Isopropyl alcohol] = $7x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.0	1.0	1.5	2.8	3.2	3.2
(5)	0.0	1.5	2.2	3.6	5.5	5.2
(8)	0.1	1.9	3.0	4.5	6.2	7.5
(10)	0.1	2.3	3.2	5.8	7.4	8.8
(13)	0.1	2.5	3.6	7.2	8.5	10.4
(15)	0.2	2.9	4.2	8.0	9.5	12.2
(20)	0.2	3.3	5.5	8.8	10.3	14.4
(25)	0.2	3.3	6.2	9.5	11.4	15.9
(30)	0.3	3.4	6.5	10.0	13.5	16.5
(35)	0.4	3.5	7.0	10.2	14.0	16.8
∞	2.0	4.0	8.0	12.0	3.2	20.0
(10^3) k_1 s^{-1}	**0.998**	**0.998**	**0.960**	**0.927**	**0.928**	**0.931**

Figures in parentheses denotes time in minutes

Table- 4.24

Variation of [S(IV)] at Ag (I) =$1.5x10^{-5}$ mol dm^{-3}, [Isopropyl alcohol] = $7x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0	1.0	1.5	2.9	3.3	3.2
(5)	0	1.4	2.2	3.7	5.6	5.2
(8)	0.1	1.6	3.0	4.6	6.2	7.5
(10)	0.1	2.3	3.2	5.8	7.4	8.8
(13)	0.1	2.6	3.6	7.2	8.5	10.4
(15)	0.2	2.8	4.2	8.3	9.9	12.2
(20)	0.2	3.2	5.6	9.0	10.4	14.6
(25)	0.3	3.3	6.7	9.5	11.4	16.0
(30)	0.4	3.6	7.0	10.7	13.6	16.9
(35)	0.4	3.6	7.2	11.0	15.2	18.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.18**	**1.13**	**1.13**	**1.15**	**1.16**	**1.15**

Figures in parentheses denotes time in minutes

Table- 4.25

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.0	0.0	0.0	0.0
(5)	0.0	0.0	0.0	0.0	0.2
(8)	0.1	0.1	0.1	0.1	0.4
(10)	0.1	0.1	0.1	0.2	0.6
(13)	0.1	0.1	0.1	0.4	0.7
(15)	0.1	0.2	0.2	0.5	0.7
(20)	0.2	0.2	0.2	0.5	0.7
(25)	0.2	0.2	0.3	0.6	0.7
(30)	0.2	0.3	0.4	0.6	0.8
(35)	0.4	0.4	0.4	0.6	0.8
∞	2.0	2.0	2.0	2.0	2.0
(10^3) k_1 s^{-1}	**0.888**	**0.998**	**1.18**	**2.08**	**2.89**

Figures in parentheses denotes time in minutes

Table- 4.26

Variation of Ag (I) at S(IV)]= 2 x10^{-3} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I), mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.5	1.0	1.0	1.0	1.5
(5)	0.8	1.5	1.4	1.4	2.0
(8)	1.2	1.9	1.6	1.8	2.6
(10)	1.5	2.3	2.3	2.5	3.0
(13)	1.7	2.5	2.6	2.9	3.2
(15)	2.2	2.9	2.8	3.2	3.3
(20)	2.5	3.3	3.2	(18) 3.4	(18) 3.4
(25)	2.9	3.3	3.3	(20) 3.6	(20) 3.8
(30)	3.0	3.4	3.6	(22) 3.8	(22) 3.9
(35)	3.4	3.5	3.6	(25) 3.8	(24) 3.9
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.859**	**0.998**	**1.13**	**2.08**	**2.45**

Figures in parentheses denotes time in minutes

Table- 4.27

Variation of Ag (I) at S(IV)]= 4 x10^{-3} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2}mol L^{-1}

Ag (I), mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	1.5	1.5	1.5	1.8	2.3
(5)	2.0	2.2	2.2	2.5	3.2
(8)	2.5	3.0	3.0	3.2	4.5
(10)	2.9	3.2	3.2	3.8	5.6
(13)	3.4	3.6	3.6	4.2	6.9
(15)	4.2	4.2	4.2	4.6	7.2
(20)	5.1	5.5	5.6	(18) 5.6	(18) 7.3
(25)	6.0	6.2	6.7	(20) 6.7	(20) 7.5
(30)	6.2	6.5	7.0	(22) 7.7	(22) 7.6
(35)	6.5	7.0	7.2	(25) 7.7	(24) 7.9
∞	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1 s^{-1}	**0.816**	**0.960**	**1.13**	**2.05**	**2.67**

Figures in parentheses denotes time in minutes

Table- 4.28

Variation of isopropyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag(I) = 5 $x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-7}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$7x10^{-5}$**	**$3x10^{-4}$**	**$8x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	0.7	0.6	0.7	0.5	0.7	0.5
(5)	0.9	1.0	1.0	0.9	1.0	0.8	1.0	0.8
(8)	1.3	1.5	1.3	1.2	1.3	1.2	1.3	0.9
(10)	1.9	1.8	1.6	1.5	1.5	1.5	1.5	1.2
(13)	2.2	2.0	1.9	1.8	1.9	1.7	1.7	1.4
(15)	2.7	2.6	2.5	2.2	2.4	2.2	2	1.6
(20)	3.3	3.3	3.3	2.6	2.7	2.5	2.3	1.9
(25)	3.5	3.5	3.3	3.0	3.0	2.9	2.5	2.0
(30)	3.5	3.5	3.4	3.3	3.2	3.0	2.6	2.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.30**	**1.28**	**1.16**	**0.945**	**0.902**	**0.859**	**0.549**	**0.426**

Figures in parentheses denotes time in minutes

Table- 4.29

Variation of isopropyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) =$1x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-7}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$7x10^{-5}$**	**$3x10^{-4}$**	**$8x10^{-4}$**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	0.7	0.7	0.8	1.0	0.7	0.7
(5)	0.9	1.0	1.1	0.9	1.1	1.5	1.0	0.9
(8)	1.3	1.5	1.5	1.3	1.3	1.9	1.3	1.2
(10)	1.9	1.8	1.8	1.5	1.5	2.3	1.5	1.5
(13)	2.2	2.1	2.0	1.8	1.9	2.5	1.7	1.7
(15)	2.7	2.7	2.5	2.2	2.4	2.9	2.2	1.9
(20)	3.3	3.3	3.3	2.6	2.7	3.3	2.4	2.1
(25)	3.5	3.5	3.4	3.3	3.2	3.3	2.6	2.3
(30)	3.7	3.6	3.5	3.5	3.4	3.4	2.9	2.5
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.47**	**1.36**	**1.24**	**1.12**	**1.03**	**0.998**	**0.711**	**0.566**

Figures in parentheses denotes time in minutes

[Isopropyl alcohol] Dependence

To know the effect of isopropyl alcohol on Ag (I) catalysed autoxidation of S(IV) Isopropyl alcohol variation was carried out from $5x10^{-7}$ mol dm^{-3} to $8x10^{-4}$ mol dm^{-3} at two different Ag (I) that is $5x10^{-6}$ mol dm^{-3} to 1 x 10^{-5} mol dm^{-3} but fixed S (IV) = $2x10^{-3}$ mol dm^{-3} at pH = 4.95 and t=30^o C. The results indicated that by increasing isopropyl alcohol the rate becomes decelerates.

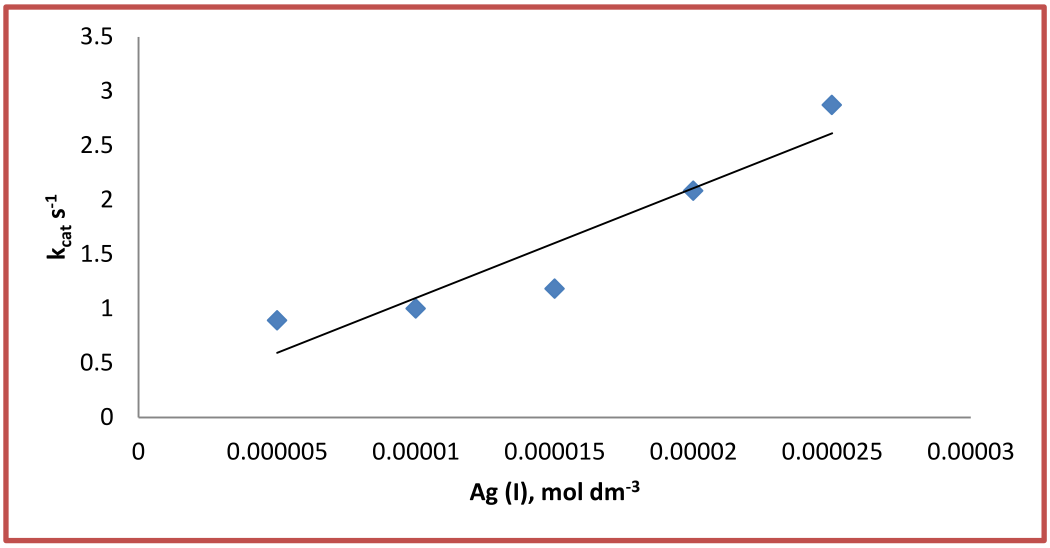


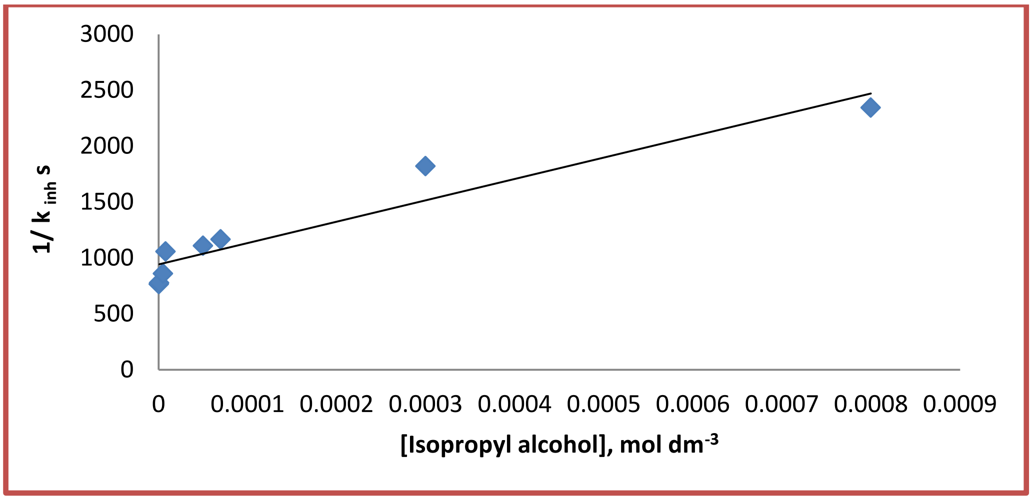
Fig.4.4 : Effect of catalyst at [S(IV)] = $2x10^{-3}$ mol dm^{-3} [Isopropyl alcohol] = $7.0x10^{-5}$ mol dm^{-3}, t= 30^o C in acetate buffered medium. The value of intercept and slope are 2.22 x 10^{-4} s and 8.5 x 10^1 mol dm^{-3} s respectively. Depending on the observed results the reaction follows the following rate law (10)

$$-d [S(IV)] /dt = (k_1+k_2[Ag(I)] [S(IV)] / 1 + B [\text{Isopropyl alcohol}] \quad (10)$$

Where $k_{inh} = (k_1+k_2[Ag(I)] / 1 + B [\text{Isopropyl alcohol}] = k_{cat}/ 1 + B [\text{Isopropyl alcohol}]$ (11)

$$1/ k_{inh} = 1 + B [\text{Isopropyl alcohol}] / k_{cat} \quad (12)$$

$$1/ k_{inh} = 1/ k_{cat} + B [\text{Isopropyl alcohol}] / k_{cat} \quad (13)$$



<u>Fig. 4.5</u> : Effect of isopropyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag(I) = $5x10^{6}$ mol dm^{-3} pH = 4.95, t = 30^{o} C in acetate buffered medium. The plot of 1/ k_{inh} v/s [Isopropyl alcohol] is linear with intercept 9.41 x 10^{2} s and slope 1.9 x 10^{6} mol dm^{-3} s from which the value of B = 2.03 $x10^{3}$ mol dm^{-3}

Table- 4.30

The values of k_{inh} at different [Isopropyl alcohol], [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	10^{3} k_{inh} s^{-1}	1/k_{inh} s
$5.0x10^{-7}$	1.30	769
$8.0x10^{-7}$	1.28	781
$5.0x10^{-6}$	1.16	862
$8.0x10^{-6}$	0.94	1064
$5.0x10^{-5}$	0.90	1111
$7.0x10^{-5}$	0.85	1176
$3.0x10^{-4}$	0.54	1852
$8.0x10^{-4}$	0.42	2381

Effect of Temperature

The values of k_{obs} were determined at three different temperatures in the range of 30^o C to 40^o C. The results are given in table 4.31. By plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 71.83 KJ mol^{-1}

Table – 4.31

Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3}, [Isopropyl alcohol] = 7.0 x 10^{-5} mol dm^{-3}, pH = 4.95

t^o C	10^3 k_{obs} s^{-1}
30	0.88
35	1.13
40	1.73

Table- 4.32

Variation of [S(IV)] at Ag (I) = 1x10^{-5} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	4	6	8	10
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.5	2.1	3.5	3.5	3.8
(5)	0.0	0.8	2.6	4.7	5.5	5.2
(8)	0.1	1.2	3.2	5.9	6.4	7.3
(10)	0.1	1.5	4.2	6.7	7.9	8.8
(13)	0.2	1.8	4.9	8.0	8.8	10.4
(15)	0.3	2.5	5.5	8.5	10.0	12.9
(20)	0.3	3.0	5.9	9.6	11.2	14.9
(25)	0.4	3.2	6.2	10.2	12.6	15.4
(30)	0.4	3.5	7.2	10.8	13.6	16.7
(35)	0.4	3.7	7.5	11.2	15.2	18.9
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.29**	**1.23**	**1.210**	**1.23**	**1.20**	**1.20**

Figures in parentheses denotes time in minutes

Table- 4.33

Variation of [S(IV)] at Ag (I) =1x10^{-5} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.9	2.8	4.5	4.5	4.6
(5)	0.0	1.2	3.6	5.5	6.5	6.4
(8)	0.1	1.9	4.9	7.2	7.8	8.2
(10)	0.2	2.2	5.7	8.2	10.5	10.5
(13)	0.2	2.6	6.4	9.5	11.2	12.6
(15)	0.3	2.9	6.7	10.2	12.5	14.6
(20)	0.3	3.2	7.2	11.2	14.5	16.0
(25)	0.5	3.7	7.5	11.5	15.2	18.9
(30)	0.5	3.9	7.8	11.6	15.5	19.2
(35)	0.6	3.9	7.8	11.7	15.6	19.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.80**	**1.87**	**1.81**	**1.84**	**1.87**	**1.83**

Figures in parentheses denotes time in minutes

Table- 4.34

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I), mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.0	0.1	0.1	0.2
(5)	0.0	0.0	0.2	0.2	0.4
(8)	0.2	0.1	0.3	0.3	0.6
(10)	0.2	0.2	0.4	0.3	0.8
(13)	0.2	0.3	0.5	0.4	0.8
(15)	0.3	0.3	0.6	0.5	0.9
(20)	0.3	0.4	0.6	0.5	0.9
(25)	0.3	0.4	0.6	0.6	1.2
(30)	0.4	0.5	0.6	0.8	1.2
(35)	0.4	0.5	0.7	1.0	1.2
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**1.13**	**1.57**	**1.92**	**2.89**	**4.48**

Figures in parentheses denotes time in minutes

Table- 4.35

Variation of Ag (I) at S(IV)] = 1x10^{-3} mol dm^{-3}, [Isopropyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I), mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.2	0.1	0.2	0.3
(5)	0.2	0.2	0.2	0.3	0.5
(8)	0.3	0.4	0.3	0.5	0.7
(10)	0.3	0.5	0.4	0.7	0.9
(13)	0.4	0.6	0.6	0.8	1.0
(15)	0.4	0.6	0.8	0.9	1.0
(20)	0.5	0.7	1.0	0.9	1.1
(25)	0.5	0.9	1.0	1.0	1.2
(30)	0.6	0.9	1.0	1.1	1.3
(35)	0.6	0.9	1.0	1.3	1.4
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**1.73**	**2.97**	**3.87**	**4.49**	**5.27**

Figures in parentheses denotes time in minutes.

Table - 4.36

Variation of isopropyl alcohol at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = $5\text{x}10^{-6}$ mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}, CH_3COOH = $3\text{x}10^{-2}$ mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	**$5\text{x}10^{-7}$**	**$8\text{x}10^{-7}$**	**$5\text{x}10^{-6}$**	**$8\text{x}10^{-6}$**	**$5\text{x}10^{-5}$**	**$7\text{x}10^{-5}$**	**$3\text{x}10^{-4}$**	**$8\text{x}10^{-4}$**
Time, (Min)	Volume of 5 x10 $^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.9	0.8	0.7	0.8	0.8	0.9	0.8
(5)	1.0	1.2	1.0	1.0	1.0	1.0	1.3	1
(8)	1.3	1.6	1.3	1.3	1.4	1.4	1.5	1.3
(10)	1.9	1.9	1.7	1.5	1.6	1.6	1.7	1.5
(15)	2.2	2.1	2.0	1.8	1.9	1.9	2.0	1.9
(20)	2.5	2.7	2.6	2.2	2.5	2.5	2.2	2.2
(25)	3.3	3.3	3.3	2.6	2.8	2.8	2.5	2.4
(30)	3.5	3.5	3.4	3.2	3.1	3.1	2.7	2.6
(35)						3.3	2.9	2.6
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.36**	**1.34**	**1.25**	**1.03**	**0.972**	**0.893**	**0.630**	**0.555**

Figures in parentheses denotes time in minutes

Table- 4.37

Variation of isopropyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 40^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$mol L^{-1}

[Isopropyl alcohol] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-7}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$7x10^{-5}$**	**$3x10^{-4}$**	**$8x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.9	1.0	0.9	0.9	0.9	0.9	1.2	1.0
(5)	1.2	1.3	1.3	1.3	1.3	1.2	1.5	1.3
(8)	1.3	1.7	1.6	1.5	1.6	1.5	1.7	1.5
(10)	1.9	2.0	1.9	1.9	1.9	1.9	2	1.9
(15)	2.2	2.4	2.1	2.2	2.2	2.2	2.3	2.2
(20)	2.5	2.7	2.6	2.5	2.6	2.4	2.5	2.5
(25)	3.4	3.3	3.3	2.9	3	2.6	2.9	2.9
(30)	3.6	3.5	3.4	3.2	3.3	2.9	3.2	3.0
(35)					3.4	3.3	3.2	3.0
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.42**	**1.41**	**1.29**	**1.16**	**1.07**	**0.916**	**0.785**	**0.689**

Figures in parentheses denotes time in minutes

DISCUSSION

In aqueous solutions SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH the following equilibrium operates

$$HSO_3^{-1} \rightleftharpoons H^+ + SO_3^{-2} \qquad (14)$$

The equilibrium constant is 5.07×10^{-7}. In the experimental range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. During the course of reaction fraction order obtain is 0.30 indicates that it is almost independent of pH which is co-relate with the work of Irena– Wilkkosz (2008)[15] Bigelow et al (1898)[4] studied the effect of alcohols on the reactions between sodium sulphite and O_2 and found that the alcohols inhibited the reaction rate. Alyea et al(1929)[20] studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Backstrom (1934)[3] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2. Grgic et al (1998)[10] studied the inhibition effect of acetate, oxlate, format on Fe-catalysed autoxidation of S(IV) at pH 2.8, 3.7,4.5 and found that oxlate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe^{+3} due to formation of complexion with oxlate. Bostjan et al (2006)[19] studied the effect of carboxylic acid on Mn (II) catalysed oxidation of S (IV) and found that mono carboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag (I) catalysed reaction is decelerated by the addition of isopropyl alcohol in the present study. Gupta et al (2008)[12] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3- 10^4. In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S (IV) by isopropyl alcohol are found to be 4.92×10^4 mol dm^{-3} and 2.03×10^3 mol dm^{-3} respectively. These values are in the same range as reported by Gupta et al. This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick and Zhang 1996[7]

$$HSO_3^{-1} \xrightleftharpoons{K_d} H^+ + SO_3^{-2} \quad K_d = 5.01 \times 10^{-7,\,18} \qquad (15)$$

$$Ag^+ + {}^-O_2CCH_3 \xrightleftharpoons{K_{oAc}} AgO_2CCH_3 \quad K_{oAc} = 2.29^{22} \qquad (16)$$

$$Ag^+ + SO_3^{-2} \xrightleftharpoons{K_1} AgOSO_2^- \quad K_1 = 2.51 \times 10^{5},^{20} \qquad (17)$$

$$Ag^+ + HSO_3^{-1} \xrightleftharpoons{K_2} AgHSO_3 \qquad (18)$$

$$AgOSO_2^- + O_2 \xrightleftharpoons{K_3} AgOSO_2^{-1}.O_2 \qquad (19)$$

$$AgHSO_3 + O_2 \xrightleftharpoons{K_4} AgHSO_3.O_2 \qquad (20)$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (21)$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \qquad (22)$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \qquad (23)$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \qquad (24)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \qquad (25)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \qquad (26)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \qquad (27)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \qquad (28)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \qquad (29)$$

$$SO_4^{-\bullet} + \text{isopropyl alcohol} \xrightarrow{k_{10}} \text{Non Chain product} \qquad (30)$$

By assuming long chain hypothesis and steady state approximation $d[SO_3^{-\bullet}]/dt$, $d[SO_4^{-\bullet}]/dt$, $d[SO_5^{-\bullet}]/dt$, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 31)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Isopropyl alcohol}]\}\,[SO_4^{-1}] \qquad (31)$$

Since the reaction is completely stopped in the presence of [Isopropyl alcohol] at 8×10^{-4} mol dm^{-3}, so the step (24) and (27) appear to be unimportant. The step (26) is ignored because the reaction is completely seized in the presence of higher concentration of isopropyl alcohol by omission and substitution from the above mechanism the following rate law can be obtain (32)

$R_{cat} = k_1 [Ag(I)][S(IV)]/\{k_9[x]+k_{10}[\text{Isopropyl alcohol}]\}$ (32)

Prasad et al (2013)[22] and Gupta et al (2008)[12] proposed a similar mechanism for the Co_2O_3 and CoO catalysed autoxidation of SO_2 inhibited by formic acid and ethanol respectively, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 2.03×10^3 mol dm^{-3} which is in the range of 10^3 -10^4 and also coincide with the reported value of B of Co_2O_3 catalysed autoxidation of S(IV) by formic acid is 3.58×10^3 mol dm^{-3} So on the basis of calculated value of B we concluded that isopropyl alcohol act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

6. **CONCLUSIONS**

The following conclusions are deduced from the results of the isopropyl alcohol inhibited Ag (I) catalysed autoxidation of S(IV) was that inhibit the oxidation with the slow influence. The value of Inhibition factor of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are in the range of 10^3-10^4 which shows that free radical mechanism is operative.

REFERENCES

1. Alyea H. N. and Backstrom, H. L. J., 1929, The inhibitive action of alcohols on the autoxidation of sodium sulfite. *Journal of American Chemical Society,* **51**, 90-107**.**
2. Ashmore P.G., 1963, Catalysis and Inhibition of Chemical Reactions, Butterworths, London.
3. Backstrom H. L. J., 1934, The chain mechanism of the autoxidation of sodium sulfite solutions. *Z. Phys. Chem.*(B), **25**, 122-138.
4. Bigelow S. L., 1988, Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.
5. Clifton C.L., Huie, R.E., 1989, Rate constants for hydrogen abstraction reactions of the sulphate radical, $SO_4^{-\cdot}$ Alcohols. *International Journal of Chemical Kinetics*, **21**, 677–687.
6. Connick R.E., Zhang, Y.-X., 1996, Kinetics and mechanism of the oxidation of HSO_3 by O_2, the manganese (II)-catalyzed reaction. Inorganic Chemistry **35**, 4613–4621.
7. Connick R.E., Zhang Y.-X., Lee S., Adamic R., Chieng, P.,1995, Kinetics and mechanism of the oxidation of HSO_3 byO_2, the uncatalyzed reaction, *Inorganic Chemistry* **34**, 4543–4553.
8. Dogliotti L., Hayon E., 1967, Flash photolysis of per sulfate ions in aqueous solutions, Study of the sulfate and ozonide radical anions. *Journal of Physical Chemistry,* **71**, 2511–2516.
9. Gilbert B.C., Stell J.K., Peet W.J., Radford K.J., 1988, Generation and reactions of the chlorine atom in aqueous solution, Journal of the Chemical Society, Faraday Transactions1, **84**, 3319–3330.
10. Grgic I., Dovzan A., Bercic G., and Hudnik V., 1998, The effect of atmospheric organic compounds on the Fe-catalyzed S(IV) autoxidation in aqueous solution, *J. Atmos. Chem.* **29**, 315–337.

11. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., 2008, *Transition metal chemistry*, **33,** 809.

12. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., 2008, Kinetics of the uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 Catalyzed autoxidation of Sulfur(IV) in alkaline medium, *Transition Metal Chemistry*, **33**, 809-817.

13. Hayon E., Treinin A., Wilf J., 1972, Electronic spectra, photochemistry and autoxidation mechanism of the sulfite bisulfite-pyrosulfite systems, The SO_2, SO_3 , SO_4 and SO_5 radicals, *Journal of the American Chemical Society*, **94**, 47–57.

14. Herrmann H., Ervens B., Jacobi H.-W., Wolke R., Nowacki P., Zellner R., 2000, a chemical aqueous phase radical mechanism for tropospheric chemistry, *Journal of Atmospheric Chemistry*, **36**, 231–284.

15. Irena Wilkosz, Maninka Anna, 2008, Mn (II) catalysed S (IV) oxidation and its inhibition by acetic acid in acidic aqueous solutions, *J Atmos Chem.*, **60**, 1-17.

16. Isidorov W.A., 2001, *Atmosphere Organic Chemistry* (Russian), Khimizdat, Sankt-Peterburg.

17. J Ziajka, W. Pasiuk-Bronikowska, 2003, Autoxidation of sulphur dioxide in the presence of alcohols under conditions related to the tropospheric aqueous phase, *Atmos. Environ*, ***37***, 3913.doi:10.1016/S1352-2310(03) 00503-X.

18. L.G. Sillen and A.E. Martell, 1964, stability constants of metal ion complex special publication no 17, The chemical soc. Burlington house London.

19. Podkrajsek B., Grgic I., and Tursic J., 2006, Influence of atmospheric carboxylic acid on catalytic oxidation of S(IV), *J of atmospheric chemistry*, **54**, 103-120.

20. R. Van Eldik, and G,M. Harris, 1980, *Inorg Chem.*, **19**, 880.

21. R.E. Connick, Y.X. Zhang, S. Lee, R. Adamic and P. Cheing, 1995, kinetics and mechanism of oxidation of HSO_3^- by O_2 the uncatalysed reactions, *Inorg. Chem.*, **34**, 4543.

22. Sameena Begam, Faiyaz Huusain, D.S.N. Prasad, 2013, Kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Pelagia research library*, **4(1)**, 122-131.
23. V.F. Toropova I.A. Sirotina and V.B. Rotanova, 1955, Uchenye Zapiski Kazanskogo Uni. 115 no.3, 53.
24. Warneck P., Ziajka J., Pasiuk-Bronikowska W., 1994, Scavengers of SO_4 in S(IV) autoxidation catalyzed by Fe. In Angeletti, G., Restelli, G. (Eds.), Proceedings of the Sixth European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, Vol.2.ECSC-E CEAEC, Luxembourg, pp.901–906.
25. Wine P.H., Tang Y., Thorn R.P., Wells J.R., 1989, Kinetics of aqueous phase reactions of the SO_4 radical with potential importance in cloud chemistry, *Journal of Geophysical Research,* **94**, 1085–1094.
26. Ziajka J., Beer F., Warneck P., 1994, Iron-catalysed oxidation of bisulphite aqueous solution, evidence for a free radical chain mechanism, *Atmospheric Environment*, **28**, 2549–2552.
27. Ziajka J., Krajewska M., Pasiuk-Bronikowska W., 2001, The role of myrtenal in the autoxidation of S(IV) under acidic conditions, In Hjorth J., Raes F., Angeletti G. (Eds.), Proceedings of the Eighth European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, CEC, JRC, Ispra, pp.CMD/AP P 1–4.
28. Ziajka J., Pasiuk-Bronikowska W., 1999, Effect of a-pinene and cis-verbenol on the rate of S(IV) oxidation catalysed by Fe, In Borrell, P.M., Borrell, P. (Eds.), Proceedings of the EUROTRAC Symposium, 98. WITPRESS, Southampton, pp. 756–761.
29. Ziajka J., Pasiuk-Bronikowska W., 2000, Myrtenol as an inhibitor of S(IV) autoxidation, In Rossi M.J., Rossi E.-M. (Eds.), Proceedings of the EC/EUROTRAC-2 Joint Workshop, EC Cluster 4, ‘‘Chemical Processes and Mechanisms’’, EUROTRAC-2, ‘‘Chemical Mechanism Development’’, EPFL, Lausanne, pp.152–155.

30. Ziajka J., Pasiuk-Bronikowska W., 2003, Fe-catalysed autoxidation of S(IV) inhibited by aliphatic alcohols, nonterpenic and substituted with a-pinene skeletal structure , In Losno R., (Ed.), Proceedings of the EC/EUROTRAC-2 Joint Workshop, EC Cluster 3 ‘‘Oxidation Processes’’, EUROTRAC-2, ‘‘Shaping the Future of Atmospheric Chemistry Research in Europe’’, University Paris, Paris.

31. Ziajka J., Pasiuk-Bronikowska W., Warneck P., 1996, The role of the sulfate radical anions in S(IV) oxidation by a chain mechanism. In, Borrell P.M., Borrell P., Cvitas T., Kelly K., Seiler W. (Eds.), Proceedings of the EUROTRAC Symposium 96, Computational Mechanics Publications, Southampton, pp. 401–405.

CHAPTER - V

Kinetics of Isoamyl Alcohol Inhibited Uncatalysed and Ag (I) Catalysed Autoxidation of S (IV) in Acidic Medium

ABSTRACT

The kinetics of atmospheric autoxidation of S(IV) by Ag (I) in the pH range 4.02-5.25 has been studied. Based on the observed results a free radical mechanism operative and following rate law has been proposed.

$$-d\,[S(IV)/dt \quad = \quad (k_1+k_2[Ag])\,[S(IV)]/\,1+\ B\,[\text{Isoamyl alcohol}]$$

INTRODUCTION

Sulphur dioxide emission results in acidic deposition which is one of the serious global problems. This process involves complex transformation of SO_2 to H_2SO_4 in gaseous and liquid phases of the atmosphere. The major reaction path is the oxidation of sulphur dioxide in the aqueous phase. It is believed that 50-80% of atmospheric sulphur dioxide reacts with in atmospheric water droplets (rain, fog and clouds) (Langner and Rodhe, 1991)[13]. Depending on conditions, three different SO_2 oxidation pathways are crucial in the atmospheric aqueous phase. These are the oxidation of dissolved SO_2 by H_2O_2, O_3 and by O_2. Oxidation by O_2 may be important in the presence of catalysts only. Potential catalysts are transition metal ions with at least two oxidation states (e.g. vanadium, chromium, manganese, iron, cobalt, nickel, cooper) (Grgic et al. 1991[6], Berglund et al. 1993[2] Brandt and van Eldik 1995[3], Berglund and Elding 1995[1], Gupta 2008[30], Manika 2008[19]) The only source of these metals in the atmospheric aqueous phase is the dissolution of aerosol particles incorporated in water droplets. The common particles containing trace metals are soil dust, fly ash from power plants, and exhaust from combustion engines and industrial operations. Dissolved in atmospheric water organic compounds such as carboxylic acids, carbonyls, alcohols, phenols, amides, amines etc. may react with sulphoxy radicals and transition metal ions, and thus alter the rate of catalytic S(IV) oxidation (Martin et al.,1991[15] Pasiuk- Bronikowska et al., 1997[16]; Grgic et al., 1998[7],1999[10], Ziajka and Pasiuk-Bronikowska, 2005[21]). The sources of organic compounds are numerous and they comprise anthropogenic and biogenic emissions and photochemical transformations of precursors in atmospheric aqueous, gaseous, and particulate phases (Chebbi and Carlier, 1996[4]), Direct anthropogenic emissions of organic compounds (e.g. from incomplete combustion of fossil fuels, wood and other biomass material) and/or photo-oxidation of anthropogenic organic compounds in the atmosphere are the main sources of these compounds in urban and industrial environments (Chebbi and Carlier,1996[4], Kawamura et al., 1996a[12]). It has been reported that automobile exhaust can be a significant source as well (Kawamura and Kaplan, 1987[11], Souza et al., 1999[18], Kawamura and Kaplan (1987)[11] found that the distribution of alcohols measured in gasoline and diesel motor exhausts is similar to that of urban air samples. Because of their low vapour pressures and high solubility in water, alcohols are predominantly present in atmospheric aerosols, cloud droplets, fog droplets and precipitation (Chebbi and Carlier, 1996[4], Souza et al.,1999[18]). Very little is known so far about the influence of alcohols on the catalytic S(IV) oxidation by O_2. In general the kinetics agreed with the rate law (1).

$$- d[S(IV)]/dt = (k_1 + k_2[H^+]^{-1}) [Catalyst] [S(IV)] \qquad (1)$$

Current laboratory studies of chemical reactions involving S(IV) species and organic ligands have focused on the iron-catalysed autoxidation (Grgic et al., 1995[5], Grgic and Poznic, 1998[8], Grgic et al., 1999[10], Wolf et al., 2000[20]) it has been found that organic ligands such as oxalate, acetate and format inhibit this process. Thus, despite the studies cited above the effect of alcohols on the metal catalyzed oxidation of S(IV) in atmospheric water is still poorly understood and more work in this area is not available. The purpose of the present work was to study the influence of isoamyl alcohol on the Ag(I) catalysed S(IV) oxidation under the conditions representative for acidic medium.

EXPERIMENTAL

The experimental procedure was exactly the same as described earlier.[22] All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature 30 ± 1^0 C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at 1600±10 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction.

For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically. The reproducibility of replicate measurements was generally better than 10 ± 1 %. All calculations were performed in MS Excel.

PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S(VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure.

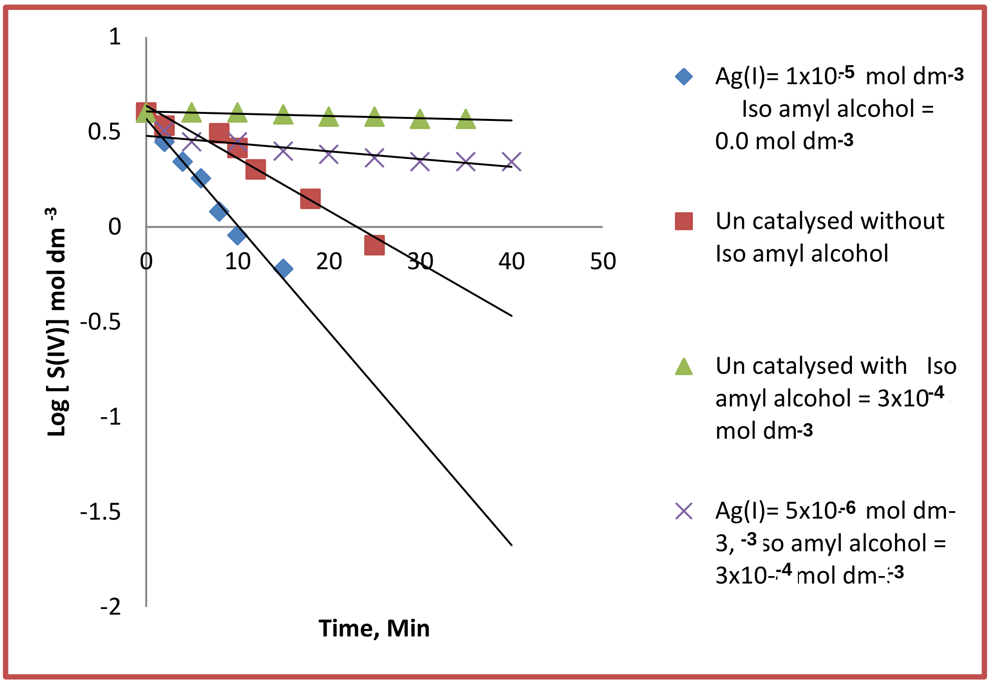
The product analysis showed the recovery of sulphate to be 98 ± 1%., in all cases in agreement with eq. (2)

$$S(IV) + 0.5\,O_2 \longrightarrow S(VI) \qquad (2)$$

RESULTS

Preliminary Investigation

The kinetics of both uncatalysed and Ag (I) catalysed and isoamyl alcohol inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30°C. In both the cases the first order dependence of S(IV) was observed in the kinetics data treatment for the determination of first order rate constant $k_1$was carried out from log [S(IV)] versus time, t. The plots were shown in fig 5.1. From the fig.5.1 observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by isoamyl alcohol.



<u>Fig. 5.1</u>, The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2x 10^{-3}, mol dm^{-3}, pH = 4.95, t = 30^{o} C.

(◇) Ag (I) = 1x 10^{-5} mol dm^{-3},[Isoamyl alcohol] = 0.0 mol dm^{-3}

(□) Uncatalysed without isoamyl alcohol

(△) Uncatalysed with [Isoamyl alcohol] = 3x10^{-4} mol dm^{-3}

(x) Ag (I) = 5x 10^{-6} mol dm^{-3}, [Isoamyl alcohol]= 3x 10^{-4} mol dm^{-3}

Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of Ag (I) and all the solutions were prepared in doubly distilled water.

Table- 5.1

Quantitative Analysis of Sulphate in Final Product Solution

10^3 [S(IV)] mol dm^{-3}	Ag (I) mol dm^{-3}	pH	10^3 [SO_4^{-2}] mol dm^{-3}	[SO_4^{-2}] /[S(IV)]	% of S(IV) recovery
5.0	0.00	4.95	4.90	0.980	98.0
5.0	$5x10^{-6}$	4.95	4.92	0.984	98.4
5.0	$1x10^{-5}$	4.95	4.95	0.990	99.0

Table– 5.2

Variation of [S(IV)] at pH = 4.95, t = 30° C, CH_3COONa = $7x10^{-2}$ mol L^{-1} CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	3	4
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot			
(0)	0.0	0.0	0.0	0.0
(2)	0.5	0.6	1.3	1.6
(8)	0.8	0.9	2.1	2.2
(10)	1.0	1.4	3.2	3.2
(12)	1.2	2.0	3.8	4.3
(18)	1.4	2.6	4.6	5.4
(25)	1.6	3.2	4.8	6.5
∞	2.0	4.0	6.0	8.0
(10^3) k_1 s^{-1}	**1.04**	**1.06**	**1.09**	**1.09**

Figures in parentheses denotes time in minutes

Dependence of S(IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range from $1x10^{-3}$ mol dm^{-3} to $4x10^{-3}$ mol dm^{-3} at pH = 4.95, t = 30^{o} C in acetate buffered medium. The kinetics was found to be first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of first order rate constant k_1 are given in table -5.2. The dependence of reaction rate on [S(IV)] follows the rate law (3)

$$-d\,[S(IV)]\,/dt = k_1\,[S(IV)] \qquad (3)$$

Table- 5.3

The values of k_1 for uncatalysed reaction at different [S(IV)], pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	**(10^3) k_1 s^{-1}**
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

[Isoamyl alcohol] Dependence

The major aim of this study was to examine the effect of isoamyl alcohol on the autoxidation of S(IV) in acetate buffer medium and varying the [Isoamyl alcohol] from $5x10^{-7}$ mol dm^{-3} to $3x10^{-4}$ mol dm^{-3}, we observed the rate of the reaction decreased by increasing [Isoamyl alcohol]. The results are given in table 5.4 However the nature of the [S(IV)] dependence in presence of isoamyl alcohol did not change and remains first order. The first order rate constant k_{inh} , in the presence of isoamyl alcohol was defined by rate law (4)

$$-d\,[S(IV)]\,/dt = k_{inh}\,[S(IV)] \qquad (4)$$

The values of k_{inh} in the presence of isoamyl alcohol decreased with increasing [isoamyl alcohol] are given in Table 5.5 which are in agreement with the rate law (5)

$$k_{inh} = k_1 / (1+B\,[\text{Isoamyl alcohol}]) \qquad (5)$$

Where B is inhibition parameter for rate inhibition by isoamyl alcohol

The equation (5) on rearrangement becomes

$$1/ k_{inh} = 1/ k_1 + B\,[\text{Isoamyl alcohol}] / k_1 \qquad (6)$$

In accordance with the equation (6) the plot of 1/ k_{inh} v/s [isoamyl alcohol] was found to be linear with non- zero intercept fig 5.2 The values of intercept (1/ k_1) and slope (B/ k_1) were found to be 1.42×10^3 s and 7.27×10^7 mol dm^{-3} s at pH = 4.95, t = 30^o C. From these values the value of inhibition parameter B was found to be 5.07×10^4 mol dm^{-3}

Table- 5.4

Variation of [Isoamyl alcohol], at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95,

t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-7}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$3x10^{-5}$**	**$5x10^{-5}$**	**$7x10^{-5}$**	**$1x10^{-4}$**	**$3x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.6	0.7	0.6	0.5	0.3	0.3	0.3	0.1	0
(10)	0.9	0.9	0.9	0.8	0.5	0.5	0.4	0.2	0
(15)	1.4	1.3	1.3	1.1	0.7	0.6	0.5	0.3	0.1
(20)	1.7	1.8	1.7	1.4	0.8	0.7	0.6	0.4	0.2
(25)	2.3	2.4	2.2	1.8	1.0	0.9	0.7	0.5	0.2
(30)	3.0	3.0	2.8	2.4	1.3	1.2	1.0	0.6	0.3
(35)	3.6	3.5	3.5	3.3	1.5	1.4	1.3	0.7	0.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**0.958**	**0.901**	**0.855**	**0.688**	**0.212**	**0.190**	**0.162**	**0.091**	**0.044**

Figures in parentheses denotes time in minute

Table - 5.5

The values of k_{inh} at different [Isoamyl alcohol], pH = 4.95, t = 30° C

$CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	$10^{3} k_{inh}$ s^{-1}	$1/k_{inh}$ s
$5.0x10^{-7}$	0.958	1044
$8.0x10^{-7}$	0.901	1110
$5.0x10^{-6}$	0.855	1170
$8.0x10^{-6}$	0.688	1453
$3.0x10^{-5}$	0.212	4717
$5.0x10^{-5}$	0.190	5263
$7.0x10^{-5}$	0.162	6173
$1.0x10^{-4}$	0.091	10989
$3.0x10^{-4}$	0.044	22727

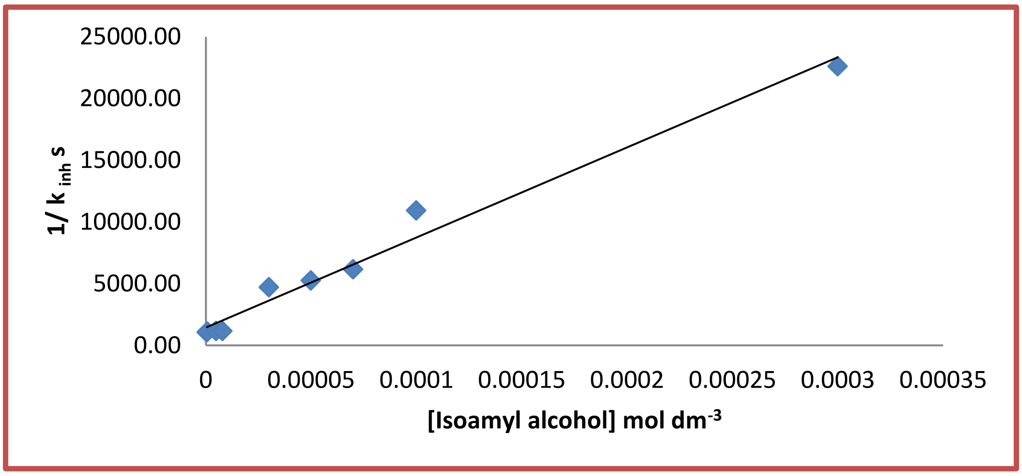


Fig.5.2 Effect of isoamyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30° C in acetate buffered medium.

Ag(I) Catalysed Reaction

At first the kinetics of Ag(I) Catalysed reaction in the absence of inhibitor was studied.

[S(IV)] Variation

The dependence of S(IV) on reaction rate was studied by varying [S(IV)] from $1\text{x}10^{-3}$ mol dm^{-3} to $10\text{x}10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5\text{x}10^{-6}$ mol $dm^{-3}$and $1\text{x}10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C. The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in fig 5.1.

Ag(I) variations

The dependence of Ag(I) on the reaction rate was studied by varying Ag(I) from $5\text{x}10^{-6}$ mol dm^{-3} to $2.5\text{x}10^{-5}$ mol dm^{-3} at S(IV) = $2\text{x}10^{-3}$ mol dm^{-3} pH= 4.95, t= 30^{o} C in acetate buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig 5.3. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law – (7)

$$-d\,[S(IV)]\,/dt \quad = \quad k_{cat}\,[S(IV)] \; = (k_1+k_2[Ag(I)]\,[S(IV)] \qquad (7)$$

$$\text{Or } k_{cat} \quad = \quad k_1+k[Ag(I)] \qquad (8)$$

From the plot in fig. 5.3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be 0.72x 10^{1} s and 8.6 x 10^{-3} mol dm^{-3} respectively at pH = 4.95, t = 30^{o} C, in acetate buffered medium.

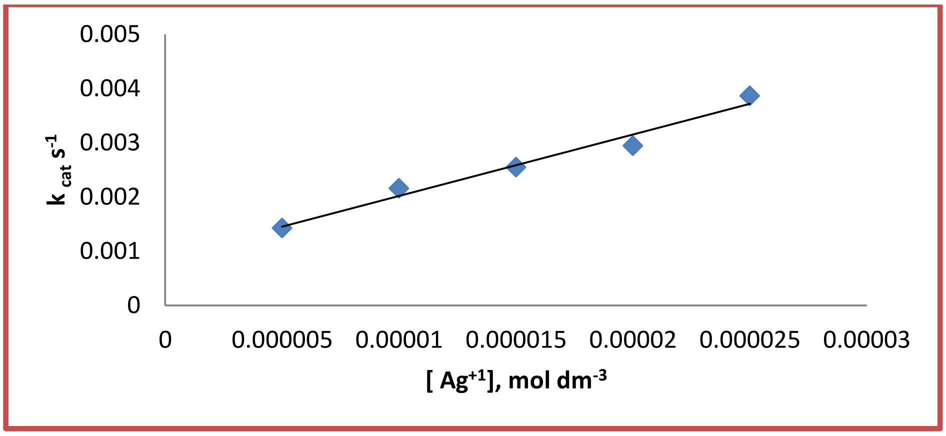


Fig.5.2 The dependence of catalyst concentration at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium.

Table - 5.6

Variation of [S(IV)] = 2x10^{-3} mol dm^{-3} at Ag (I) =5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.8	1.5	2.0	2.2
(4)	0.4	1.0	1.7	2.4	3.3	4.5
(6)	0.6	1.2	2.7	3.0	4.5	6.5
(8)	0.9	1.5	3.6	4.0	7.0	9.8
(10)	1.2	1.7	5.0	5.5	9.3	12.1
(15)	1.4	3.0	5.5	9.0	11.5	14.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3})k_1 s^{-1}	**1.43**	**1.42**	**1.41**	**1.44**	**1.46**	**1.50**

Figures in parentheses denotes time in minutes.

Table- 5.7

Variation of [S(IV)] = $2x10^{-3}$ mol dm^{-3} at Ag (I) = $1x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.9	3.0	4.5	5.6
(4)	0.8	1.8	2.8	4.8	6.3	7.8
(6)	1.2	2.2	3.6	5.9	7.8	9.5
(8)	1.4	2.8	4.5	7.8	8.9	10.2
(10)	1.5	3.1	5.0	8.9	12.5	12.8
(15)	1.7	3.4	7.0	10.3	13.6	17.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**2.19**	**2.15**	**2.15**	**2.18**	**2.14**	**2.10**

Figures in parentheses denotes time in minutes.

Table- 5.8

Variation of Ag (I) at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5x10^{-6}$**	**$1x10^{-5}$**	**$1.5x10^{-5}$**	**$2x10^{-5}$**	**$2.5x10^{-5}$**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.4	2.5	2.4
(4)	1.0	1.8	1.8	2.7	2.5
(6)	1.2	2.2	2.0	2.9	3.0
(8)	1.5	2.8	2.2	3.7	3.5
(10)	1.7	3.1	3.4		
(15)	3.0	3.4			
∞	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.42**	**2.15**	**2.54**	**2.94**	**3.88**

Figures in parentheses denotes time in minutes.

Table - 5.9

The values of k_{cat} at different concentration of Ag (I) mol dm^{-3}, pH = 4.95, t = 30^o C, CH$_3$COONa = 7x10^{-2} mol L^{-1} CH$_3$COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	$10^3 k_{cat}$ s^{-1}
0.000005	1.42
0.00001	2.15
0.00015	2.54
0.00020	2.94
0.00025	3.88

Variation of pH

Variation of pH was carried out from 4.02- 5.25 at different [S(IV), Ag (I), [Isoamyl alcohol] and temperatures. The rate decreases slightly by varying pH is inverse H$^+$ ion dependence was observed. From the plot of log k_1 v/s log (H$^+$), the order with respect to H$^+$ is 0.21 which is a fractional order and can be neglected as shown in fig 5.4.

Table -5.10

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Isoamyl alcohol] = 7.0x10^{-5} mol dm^{-3}, t = 30^o C, CH$_3$COONa = 7x10^{-2} mol L^{-1}

pH	10^3 k s^{-1}
4.02	0.172
4.35	0.214
4.56	0.272
4.75	0.328
4.95	0.373
5.25	0.422

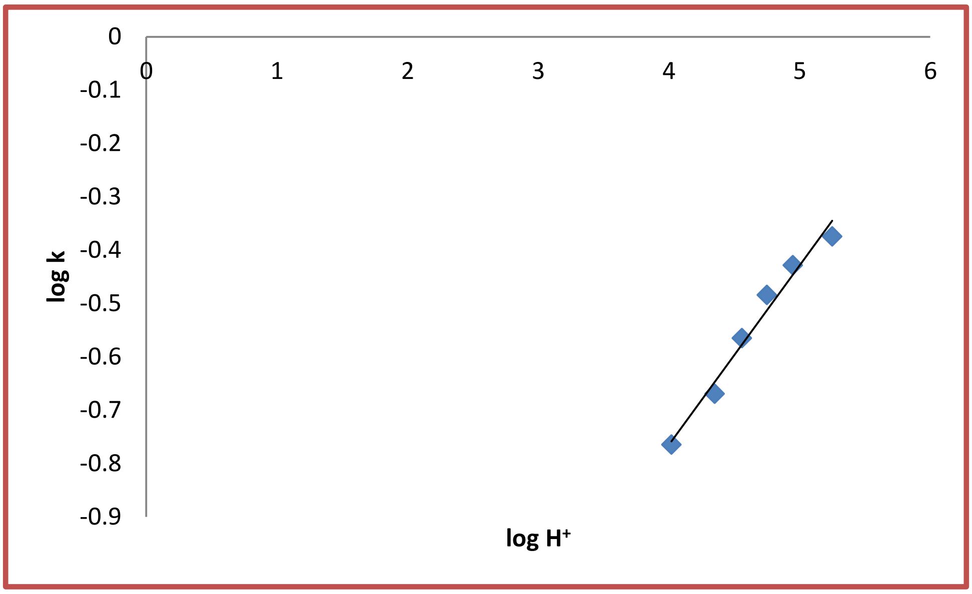


Fig.5.4 Effect of pH at [S(IV)] = 2x10^{-3} mol dm^{-3} Ag (I) = 5x10^{-6} mol dm^{-3}, [Isoamyl alcohol] = 7.0x10^{-5} mol dm^{-3}, t = 30° C in acetate buffered medium.

Table - 5.11

Rate of Ag (I) catalysed autoxidation in the presence of isoamyl alcohol.

[Isoamyl alcohol], mol dm^{-3}	Ag (I) =5x10^{-6} mol dm^{-3}	Ag (I) =1 x 10^{-5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.02			
7.0 x 10^{-5}	0.172 x 10^{-3}	0.272 x 10^{-3}	0.422 x 10^{-3}
1.0x 10^{-4}	0.123 x 10^{-3}	_	_
3.0 x 10^{-4}	0.090 x 10^{-3}	_	_
pH = 4.50			
7.0 x 10^{-5}	0.338 x 10^{-3}	0.544 x 10^{-3}	0.826 x 10^{-3}
1.0x 10^{-4}	0.186 x 10^{-3}	_	_
3.0x 10^{-4}	0.125 x 10^{-3}	_	_
pH = 5.25			
7.0 x 10^{-5}	0.437 x 10^{-3}	0.614x 10^{-3}	0.921 x 10^{-3}
1.0x 10^{-4}	0.289 x 10^{-3}	_	_
3.0x 10^{-4}	0.252 x 10^{-3}	_	_

Table - 5.12
Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of isoamyl alcohol.

[Isoamyl alcohol] 7.0 x 10^{-5} mol dm^{-3}	Ag (I) = 5x10^{-6} mol dm^{-3}	Ag (I) =1 x 10^{-5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.50			
	8.26	**7.90**	**6.02**

Table - 5.13
Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, t = 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.6	0.7	0.8	0.8
(5)	0.4	0.8	0.9	0.9	1.2	1.4
(10)	0.6	1.2	1.2	1.1	1.2	2.0
(15)	0.8	1.4	1.6	1.4	1.5	2.1
(20)	0.9	1.5	1.8	1.5	1.8	2.2
(25)	1.0	1.6	1.9	1.8	2.0	2.3
(30)	1.1	1.6	1.9	2.0	2.3	2.3
(35)	1.2	1.7	2.0	2.2	2.4	2.8
(40)	1.4	1.7	2.0	2.4	2.5	2.8
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3)k_1, s^{-1}	**0.161**	**0.212**	**0.272**	**0.334**	**0.372**	**0.432**

Figures in parentheses denotes time in minutes

Table - 5.14

Variation of pH at [S(IV)] = $4x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, t= 30^o C, CH_3COONa = $7x10^{-2}$mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.8	0.8	0.9	1.0	1.2
(5)	0.9	1.3	1.2	1.5	1.5	1.6
(10)	1.2	1.7	1.5	2.0	2.1	2.2
(15)	1.5	2.2	2.1	2.4	2.7	2.7
(20)	1.8	2.8	2.6	3.0	3.4	3.4
(25)	1.9	3.0	3.0	3.4	4.0	4.1
(30)	2.3	3.1	3.2	3.9	4.3	4.4
(35)	2.5	3.2	3.6	4.3	4.4	5.0
(40)	2.9	3.3	4.2	4.6	4.9	5.2
∞	8.0	8.0	8.0	8.0	8.0	8.0
(10^3) k_1, s^{-1}	**0.163**	**0.213**	**0.276**	**0.334**	**0.373**	**0.420**

Figures in parentheses denotes time in minutes

Table - 5.15

Variation of pH at [S(IV)] = $6x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.2	1.5	1.7	1.8	2.1	2.3
(5)	1.5	1.9	2.3	2.4	2.8	3.0
(10)	1.9	2.3	3.0	3.3	3.5	3.7
(15)	2.4	2.7	3.4	4.0	4.6	4.6
(20)	3.2	3.2	4.0	4.5	5.4	5.5
(25)	3.9	3.5	4.6	5.0	6.2	6.5
(30)	4.0	4.0	5.2	5.8	6.8	7.0
(35)	4.1	4.7	5.8	6.3	6.9	7.2
(40)	4.1	5.7	6.3	7.2	7.4	8.2
∞	12.0	12.0	12.0	12.0	12.0	12.0
(10^{3}) k_1, s^{-1}	**0.172**	**0.214**	**0.272**	**0.328**	**0.373**	**0.422**

Figures in parentheses denotes time in minute

Table - 5.16

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 1×10^{-5} mol dm^{-3}, [Isoamyl alcohol] = 7×10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.6	0.9	0.7	1.2	1.2
(5)	0.8	0.9	1.2	1.2	1.9	1.8
(10)	1.2	1.3	1.5	1.6	2.4	2.5
(15)	1.3	1.6	1.9	2.0	2.8	2.9
(20)	1.5	2.0	2.3	2.3	3.0	3.1
(25)	1.8	2.3	2.5	2.7	3.0	3.2
(30)	2.0	2.6	2.9	3.0	3.2	3.2
(35)	2.3	2.7	2.9	3.0	3.3	3.4
(40)	2.3	2.7	2.9	3.2	3.4	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.338**	**0.483**	**0.544**	**0.648**	**0.706**	**0.826**

Figures in parentheses denotes time in minutes

Table - 5.17

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 1.5x10^{-5} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.9	0.8	0.9	0.9	1.2	1.3
(5)	1.3	1.2	1.3	1.3	1.9	1.8
(10)	1.6	1.6	1.5	1.8	2.4	2.5
(15)	2.0	2.0	2.0	2.3	2.8	2.9
(20)	2.3	2.3	2.4	2.6	3.2	3.2
(25)	2.5	2.4	2.7	2.9	3.2	3.3
(30)	2.6	2.6	3.0	3.0	3.3	3.4
(35)	2.6	2.9	3.0	3.2	3.4	3.4
(40)	2.7	3.0	3.1	3.4	3.6	3.7
∞	4.0	4.0	4.0	4.0	4.0	4.0
$(10^{3})\ k_1$, s^{-1}	**0.437**	**0.533**	**0.614**	**0.730**	**0.849**	**0.921**

Figures in parentheses denotes time in minutes

Table - 5.18

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = $1x10^{-4}$ mol dm^{-3}, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.3	0.4	0.6	0.8	0.8
(5)	0.3	0.4	0.6	0.8	1.0	0.9
(10)	0.4	0.5	0.8	0.9	1.1	1.3
(15)	0.5	0.6	0.9	1.0	1.2	1.5
(20)	0.8	0.8	1.2	1.3	1.3	1.6
(25)	0.8	0.8	1.3	1.5	1.5	1.6
(30)	0.8	1.0	1.4	1.6	1.6	1.9
(35)	1.0	1.2	1.5	1.8	1.8	1.9
(40)	1.1	1.4	1.5	1.9	2.3	2.4
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.123**	**0.152**	**0.186**	**0.236**	**0.255**	**0.289**

Figures in parentheses denotes time in minutes

Table - 5.19

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = $3x10^{-4}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.0	0.3	0.3	0.4	0.5	0.8
(5)	0.2	0.3	0.4	0.5	0.6	1.0
(10)	0.3	0.4	0.6	0.7	0.7	1.5
(15)	0.5	0.5	0.8	0.9	0.8	1.9
(20)	0.6	0.6	0.9	1.0	0.8	1.9
(25)	0.6	0.6	0.9	1.3	0.9	1.9
(30)	0.6	0.8	1.0	1.5	1.3	2.0
(35)	0.7	1.0	1.0	1.5	1.5	2.0
(40)	0.8	1.0	1.2	1.6	2.0	2.0
∞	4.0	4.0	4.0	4.0	4.0	4.0
$(10^{3})k_1$, s^{-1}	**0.09**	**0.107**	**0.125**	**0.195**	**0.215**	**0.252**

Figures in parentheses denotes time in minutes

Table - 5.20

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, t= 35° C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.7	0.8	0.7	0.8	0.8
(5)	0.7	1.0	1.0	1.0	1.2	1.4
(10)	0.9	1.5	1.3	1.3	1.5	1.9
(15)	1.2	1.7	1.7	1.6	1.8	2.3
(20)	1.5	2.0	2.0	2.0	2.0	2.6
(25)	1.6	2.1	2.3	2.3	2.3	2.8
(30)	1.6	2.2	2.5	2.5	2.6	3.0
(35)	1.7	2.3	2.5	2.7	2.9	3.1
(40)	1.8	2.3	2.6	2.9	3.0	3.1
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.230**	**0.337**	**0.424**	**0.501**	**0.532**	**0.620**

Figures in parentheses denotes time in minutes

Table - 5.21

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3} Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, t= 40^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	1.0	0.7	0.9	0.8
(5)	0.9	1.2	1.5	1.2	1.3	1.4
(10)	1.0	1.6	1.9	1.6	1.6	1.9
(15)	1.3	1.9	2.3	1.9	2.0	2.3
(20)	1.5	2.1	2.5	2.1	2.3	2.6
(25)	1.6	2.3	2.7	2.4	2.5	2.8
(30)	1.8	2.5	3.0	2.9	2.9	3.2
(35)	2.1	2.6	3.0	3.0	3.2	3.3
(40)	2.4	2.6	3.0	3.2	3.4	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.314**	**0.415**	**0.561**	**0.624**	**0.708**	**0.848**

Figures in parentheses denotes time in minutes

Table- 5.22

Variation of [S(IV)] at Ag (I) = 5 x10^{-6} mol dm^{-3} , [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30°C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.8	1.0	2.1	2.5	2.4
(5)	0.4	1.2	1.5	2.8	3.2	4.5
(10)	0.6	1.2	2.1	3.5	4.2	6.2
(15)	0.8	1.5	2.7	4.6	5.9	8.5
(20)	0.9	1.8	3.4	5.4	6.8	9.8
(25)	0.9	2.0	4.0	6.2	8.1	10.3
(30)	0.9	2.3	4.3	6.8	9.1	11.5
(35)	1.1	2.4	4.4	6.9	9.3	11.8
(40)	1.3	2.5	4.9	7.4	9.4	11.9
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.365**	**0.371**	**0.373**	**0.373**	**0.372**	**0.378**

Figures in parentheses denotes time in minutes

Table- 5.23

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$mol dm^{-3} [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	4	6	8	10
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	1.2	1.2	2.5	2.6	3.4
(5)	0.4	1.9	1.6	3.4	3.5	5.1
(10)	0.7	2.4	2.4	4.2	4.8	7.2
(15)	0.9	2.8	2.9	5.5	6.2	9.2
(20)	1.1	3.0	3.5	6.4	7.8	10.9
(25)	1.2	3.0	4.2	7.2	9.5	13.2
(30)	1.5	3.2	4.9	7.8	11.3	15.3
(35)	1.6	3.3	5.7	9.2	12.6	15.9
(40)	1.6	3.4	7.1	10.5	13.3	16.2
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.707**	**0.706**	**0.706**	**0.708**	**0.706**	**0.708**

Figures in parentheses denotes time in minutes

Table- 5.24

Variation of [S(IV)] at Ag (I) =2 x10^{-5} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.3	1.2	1.5	2.6	2.8	3.8
(5)	0.5	1.9	2.3	3.5	3.6	5.5
(10)	0.9	2.4	3.2	4.8	5.2	7.8
(15)	1.3	2.8	3.5	5.7	6.6	9.9
(20)	1.4	3.2	4.0	6.9	8.2	11.2
(25)	1.5	3.2	4.4	7.7	9.8	13.5
(30)	1.5	3.3	5.4	8.4	11.4	15.6
(35)	1.6	3.4	6.5	9.5	13.2	16.6
(40)	1.8	3.6	7.4	11.1	14.4	17.8
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.841**	**0.845**	**0.843**	**0.844**	**0.842**	**0.846**

Figures in parentheses denotes time in minutes

Table- 5.25

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I), mol dm^{-3}	5x10^{-6}	1x10^{-5}	1.5x10^{-5}	2x10^{-5}	2.5x10^{-5}
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.2	0.3	0.4	0.5
(5)	0.4	0.4	0.5	0.7	0.7
(10)	0.6	0.7	0.9	1.1	0.9
(15)	0.8	0.9	1.3	1.4	1.1
(20)	0.9	1.1	1.4	1.6	1.5
(25)	0.9	1.2	1.5	1.7	1.6
(30)	0.9	1.5	1.5	1.7	1.7
(35)	1.1	1.6	1.6	1.8	1.8
(40	1.3	1.6	1.8	1.8	1.9
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.365**	**0.707**	**0.841**	**0.998**	**1.13**

Figures in parentheses denotes time in minutes

Table- 5.26

Variation of Ag (I) at S(IV)]= 2 x10^{-3} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{0} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.8	1.2	1.2	1.3	1.3
(5)	1.2	1.9	1.9	2.2	2.2
(10)	1.2	2.4	2.4	2.6	2.6
(15)	1.5	2.8	2.8	2.9	2.9
(20)	1.8	3.0	3.2	3.0	3.0
(25)	2.0	3.0	3.2	3.1	3.4
(30)	2.3	3.2	3.3	3.3	3.6
(35)	2.4	3.3	3.4	3.5	3.7
(40	2.5	3.4	3.6	3.8	3.8
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.371**	**0.706**	**0.845**	**0.965**	**1.13**

Figures in parentheses denotes time in minutes

Table - 5.27

Variation of Ag (I) at S(IV)]= 4 x10^{-3} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	1.0	1.2	1.5	1.6	1.6
(5)	1.5	1.6	2.3	2.4	2.4
(10)	2.1	2.4	3.2	3.5	3.5
(15)	2.7	2.9	3.5	4.2	4.2
(20)	3.4	3.5	4.0	5.3	5.5
(25)	4.0	4.2	4.4	5.7	6.2
(30)	4.3	4.9	5.4	6.3	7.1
(35)	4.4	5.7	6.5	6.8	7.3
(40	4.9	7.1	7.4	7.4	7.4
∞	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1 s^{-1}	**0.373**	**0.706**	**0.843**	**0.945**	**1.11**

Figures in parentheses denotes time in minutes

Table- 5.28

Variation of isoamyl alcohol at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) =5 x10^{-6} mol dm^{-3}, pH = 4.95, t= 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	**5x10^{-7}**	**8x10^{-7}**	**5x10^{-6}**	**8x10^{-6}**	**3x10^{-5}**	**5x10^{-5}**	**7x10^{-5}**	**1x10^{-4}**	**3x10^{-4}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.6	1.5	1.5	1.3	1.4	1.5	1.2	1.2	1.2
(10)	1.8	1.8	1.8	1.7	1.6	2.2	1.2	1.2	1.2
(15)	2.2	2.0	2.2	2.2	2.2	2.5	1.5	1.5	1.5
(20)	2.8	2.5	2.6	2.7	2.5	2.6	1.8	1.8	1.6
(25)	3.2	2.7	2.9	3.0	2.9	2.7	2.0	1.9	1.7
(30)	3.6	2.9	3.2	3.1	3.1	2.8	2.3	2.0	1.8
(35)	3.7	3.5	3.4	3.3	3.3	3.2	2.4	2.0	1.8
(40)	3.8	3.8	3.7	3.6	3.4	3.6	2.5	2.1	1.8
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.24**	**1.03**	**0.953**	**0.873**	**0.776**	**0.699**	**0.371**	**0.267**	**0.205**

Figures in parentheses denotes time in minutes

Table- 5.29

Variation of isoamyl alcohol at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) =$1\text{x}10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}, CH_3COOH= $3\text{x}10^{-2}$mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	**$5\text{x}10^{-7}$**	**$8\text{x}10^{-7}$**	**$5\text{x}10^{-6}$**	**$8\text{x}10^{-6}$**	**$3\text{x}10^{-5}$**	**$5\text{x}10^{-5}$**	**$7\text{x}10^{-5}$**	**$1\text{x}10^{-4}$**	**$3\text{x}10^{-4}$**
Time, (Min)	Volume of 5 $\text{x}10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.7	1.7	1.5	1.4	1.2	1.1	1.0	0.8	0.8
(10)	2.0	1.9	1.8	1.7	1.5	1.4	1.3	1.2	1.1
(15)	2.3	2.3	2.2	2.1	2.0	1.8	1.5	1.4	1.3
(20)	2.7	2.6	2.7	2.5	2.3	2.0	1.8	1.7	1.6
(25)	3.3	2.9	2.9	2.8	2.5	2.2	2.0	2.0	2.0
(30)	3.7	3.6	3.5	3.3	2.9	2.4	2.2	2.2	2.2
(35)	3.8	3.7	3.6	3.5	3.3	2.6	2.4	2.4	2.4
(40)	3.9	3.8	3.6	3.6	3.5	3.6	3.6	3.3	3.1
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
$(10^{3})\ k_1\ s^{-1}$	**1.48**	**1.21**	**1.00**	**0.944**	**0.800**	**0.715**	**0.674**	**0.566**	**0.516**

Figures in parentheses denotes time in minutes

[Isoamyl Alcohol] Dependence

To know the effect of isoamyl alcohol on Ag (I) catalysed autoxidation of S(IV) isoamyl alcohol variation was carried out from 5x10^{-7} mol dm^{-3} to 8 x 10^{-4} mol dm^{-3} at two different Ag (I) that is 5 x 10^{-6} mol dm^{-3} to 1 x 10^{-5} mol dm^{-3} but fixed S(IV) = 2x10^{-3} mol dm^{-3} at pH= 4.95 and t= 30^{o} C. The results indicated that by increasing isoamyl alcohol the rate becomes decelerates.

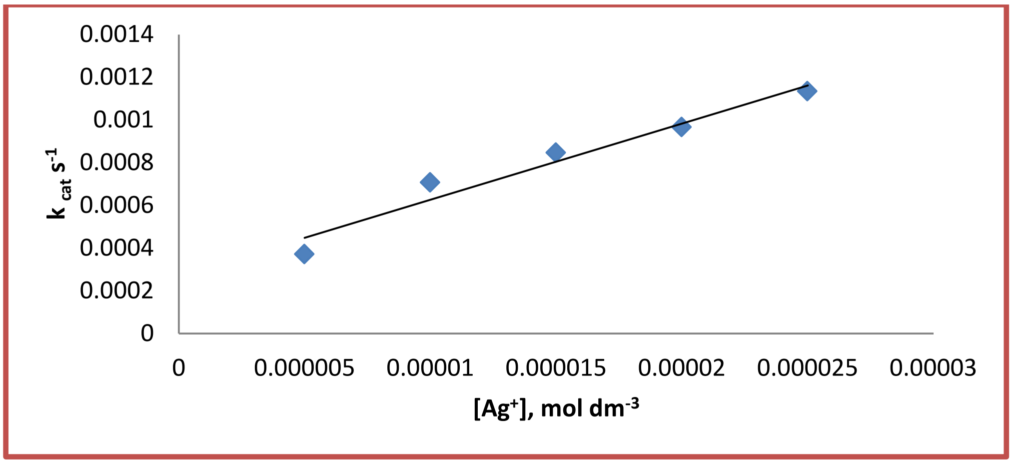


Fig.5.4 Effect of catalyst at [S(IV)]= 2x10^{-3} mol dm^{-3}, [isoamyl alcohol] = 7.0x10^{-5} mol dm^{-3}, t= 30^{o} C in acetate buffered medium. The value of intercept and slope are 2.70 x 10^{-4} s and 3.5 x 10^{1} mol dm^{-3} s respectively. Depending on the observed results the reaction follows the following rate law (9)

$$-d\,[S(IV)]\,/dt \quad = \quad (k_1+k_2[Ag(I)]\,[S(IV)]\,/\,1 + B\,[\text{Isoamyl alcohol}] \quad (9)$$

Where k_{inh} = $(k_1+k_2[Ag(I)]\,/\,1 + B\,[\text{Isoamyl alcohol}] = k_{cat}\,/\,1 + B$

[Isoamyl alcohol] (10)

$$1/\ k_{inh} = 1 + B\,[\text{Isoamyl alcohol}]\ /\ k_{cat} \quad (11)$$

$$1/\ k_{inh} = 1/\,k_{cat} + B\,[\text{Isoamyl alcohol})\,/\ k_{cat} \quad (12)$$

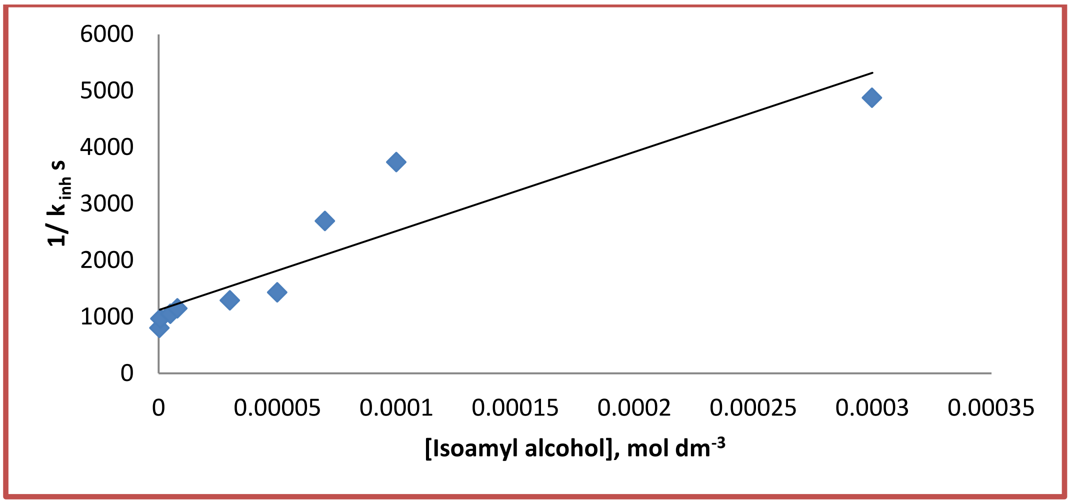


Fig.5.5 Effect of isoamyl alcohol at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3} pH = 4.95, t = 30° C in acetate buffered medium. The Plot of 1/ k$_{inh}$ v/s [isoamyl alcohol] is linear with intercept 1.12 x 10^{4} s and slope 1.39 x 10^{7} mol dm^{-3} s from which the value of B = 1.24 x10^{4} mol dm^{-3}

Table- 5.30

The values of k$_{inh}$ at different [Isoamyl alcohol], [S(IV)] = 2x10^{-3} mol dm^{-3} Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30° C CH_3COONa = 7x10^{-2}mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	10 ^{3}k$_{inh}$ s^{-1}	1/k$_{inh}$ s
5.0x10^{-7}	1.24	806
8.0x10^{-7}	1.03	971
5.0x10^{-6}	0.953	1049
8.0x10^{-6}	0.873	1145
3.0x10^{-5}	0.776	1289
5.0x10 $^{-5}$	0.699	1431
7.0x10^{-5}	0.371	2695
1.0x10^{-4}	0.267	3745
3.0x10^{-4}	0.205	4878

Effect of Temperature

The values of k_{obs} were determined at three different temperatures in the range of 30^o C to 40^o C, the results are given in table 5.31 By plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 45.16 KJ mol^{-1}

Table – 5.31

Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3}, [Isoamyl alcohol] = 7.0 x 10^{-5} mol dm^{-3}, pH = 4.95

t^o C	10^3 k_{obs} s^{-1}
30	0.373
35	0.458
40	0.605

Table - 5.32

Variation of [S(IV)] at Ag (I) =1×10^{-5} mol dm^{-3}, [Isoamyl alcohol] = 7×10^{-5} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH= 3×10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.3	0.9	1.2	2.5	2.9	2.6
(5)	0.5	1.3	1.7	3.2	3.7	4.8
(10)	0.7	1.5	2.5	4.2	4.7	6.6
(15)	0.9	1.9	3.0	5.0	6.4	8.8
(20)	1.1	2.1	3.6	5.5	7.3	10.2
(25)	1.2	2.3	4.4	6.6	8.5	11.3
(30)	1.3	2.5	4.8	7.2	9.5	12.0
(35)	1.3	2.6	5.2	8.1	10.2	13.4
(40)	1.3	2.9	5.4	8.3	11.3	13.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.453**	**0.458**	**0.456**	**0.453**	**0.459**	**0.464**

Figures in parentheses denotes time in minutes

Table - 5.33

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$ mol dm^{-3} [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.1	1.4	2.6	3.2	3.4
(5)	0.6	1.4	2.1	3.5	4.5	5.5
(10)	0.8	1.6	2.6	4.7	5.6	7.2
(15)	1.0	1.9	3.5	5.5	6.8	9.2
(20)	1.2	2.2	3.9	6.2	7.6	11.2
(25)	1.3	2.4	4.8	7.2	8.8	12.0
(30)	1.3	2.7	5.4	8.2	10.4	13.4
(35)	1.5	3.0	6.1	9.2	11.6	14.5
(40)	1.6	3.3	6.2	9.5	13.2	16.0
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.603**	**0.605**	**0.606**	**0.606**	**0.608**	**0.601**

Figures in parentheses denotes time in minutes

Table - 5.34

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Isoamyl alcohol] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.3	0.3	0.5	0.5	0.8
(5)	0.5	0.5	0.7	0.8	1.0
(10)	0.7	0.8	1.0	1.2	1.3
(15)	0.8	1.0	1.2	1.5	1.5
(20)	0.9	1.3	1.4	1.7	1.6
(25)	1.0	1.4	1.5	1.8	1.8
(30)	1.2	1.6	1.7	1.8	1.9
(35)	1.2	1.6	1.7	1.8	1.9
(40)	1.4	1.7	1.8	1.9	1.9
∞	2.0	2.0	2.0	2.0	2.0
(10^{3})k_1 s^{-1}	**0.433**	**0.787**	**0.903**	**1.18**	**1.29**

Figures in parentheses denotes time in minutes

Table- 5.35

Variation of Ag (I) at S(IV)] = $1x10^{-3}$ mol dm^{-3}, [Isoamyl alcohol] = $7x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5x10^{-6}$**	**$1x10^{-5}$**	**$1.5x10^{-5}$**	**$2x10^{-5}$**	**$2.5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.4	0.6	0.6	0.9
(5)	0.6	0.6	0.8	0.9	1.2
(10)	0.8	0.9	1.0	1.3	1.4
(15)	1.0	1.1	1.3	1.6	1.6
(20)	1.2	1.4	1.5	1.8	1.7
(25)	1.3	1.5	1.6	1.8	1.8
(30)	1.4	1.7	1.7	1.9	1.9
(35)	1.5	1.7	1.8	1.8	
(40)	1.5	1.7	1.9		
∞	2.0	2.0	2.0	2.0	2.0
$(10^3)k_1$ s^{-1}	**0.574**	**0.850**	**1.10**	**1.30**	**1.43**

Figures in parentheses denotes time in minutes

Table- 5.36

Variation of isoamyl alcohol at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5 x10^{-6} mol dm^{-3} , pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	**5x10^{-7}**	**8x10^{-7}**	**5x10^{-6}**	**8x10^{-6}**	**3x10^{-5}**	**5x10^{-5}**	**7x10^{-5}**	**1x10^{-4}**	**3x10^{-4}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.7	1.6	1.6	1.4	1.5	1.6	1.6	1.6	1.6
(10)	2.0	1.9	1.9	1.8	1.7	2.3	1.8	1.8	1.8
(15)	2.3	2.2	2.3	2.3	2.3	2.6	2.2	2.2	2.0
(20)	3.0	2.6	2.7	2.9	2.6	2.9	2.4	2.4	2.2
(25)	3.2	2.8	3.2	3.1	3.0	3.0	2.6	2.5	2.4
(30)	3.7	3.2	3.4	3.2	3.2	3.2	2.9	2.8	2.6
(35)	3.8	3.6	3.6	3.4	3.4	3.4	3.2	3.0	3.0
(40)	3.8	3.9	3.8	3.7	3.6	3.5	3.4	3.0	3.0
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.32**	**1.24**	**1.14**	**0.967**	**0.896**	**0.712**	**0.695**	**0.531**	**0.516**

Figures in parentheses denotes time in minutes

Table- 5.37

Variation of isoamyl alcohol at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) =5 $x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Isoamyl alcohol] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-7}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$3x10^{-5}$**	**$5x10^{-5}$**	**$7x10^{-5}$**	**$1x10^{-4}$**	**$3x10^{-4}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot								
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	1.8	1.8	1.7	1.5	1.6	1.7	1.8	1.7	1.7
(10)	2.2	2.2	2.0	2.0	1.9	2.4	2.2	1.9	2.0
(15)	2.4	2.6	2.4	2.4	2.4	2.7	2.4	2.3	2.2
(20)	3.2	3.0	2.8	3.0	2.6	3.0	2.6	2.6	2.4
(25)	3.4	3.2	3.3	3.2	3.2	3.2	3.0	2.7	2.6
(30)	3.8	3.7	3.6	3.4	3.4	3.3	3.2	3.0	2.8
(35)	3.8	3.8	3.7	3.6	3.5	3.5	3.3	3.2	3.2
(40)					3.6	3.6	3.4	3.3	3.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.46**	**1.33**	**1.20**	**1.05**	**0.95**	**0.799**	**0.728**	**0.660**	**0.634**

Figures in parentheses denotes time in minutes

DISCUSSION

In aqueous solutions SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH the following equilibrium operates

$$HSO_3^{-1} \rightleftharpoons H^+ + SO_3^{-2} \qquad (13)$$

The equilibrium constant is 5.07x 10^{-7} In the experimental range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. During the course of reaction fraction order obtain is 0.30 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz (2008)[19], Bigelow et al (1898)[23] studied the effect of alcohols on the reactions between sodium sulphite and O_2 and found that the alcohols inhibited the reaction rate. Alyea et al (1929)[24] studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Backstrom (1934)[28] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2. Grgic et al (1998)[7] studied the inhibition effect of acetate, oxlate, format on Fe- catalysed autoxidation of S(IV) at pH 2.8, 3.7,4.5 and found that oxlate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe^{+3} due to formation of complexion with oxlate. Bostjan et al (2006)[17] studied the effect of carboxylic acid on Mn (II) catalysed oxidation of S (IV) and found that mono carboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag (I) catalysed reaction is decelerated by the addition of isoamyl alcohol in the present study. Gupta et al (2008)[30] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3- 10^4 In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S(IV) by isoamyl alcohol are found to be 5.07 x 10^4 mol dm^{-3} and 1.24 x 10^4 mol dm^{-3} respectively. These values are in the same range as reported by Gupta et al. This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick and Zhang (1996)[29]

$$HSO_3^{-1} \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{-2} \quad K_d = 5.01 \text{ x } 10^{-7\,,\,25} \tag{14}$$

$$Ag^+ + {}^-O_2CCH_3 \overset{K_{oAc}}{\rightleftharpoons} AgO_2CCH_3 \quad K_{oAc} = 2.29^{26} \tag{15}$$

$$Ag^+ + SO_3^{-2} \overset{K_1}{\rightleftharpoons} AgOSO_2^- \quad K_1 = 2.51\text{x } 10^{\,5},^{27} \tag{16}$$

$$Ag^+ + HSO_3^{-1} \overset{K_2}{\rightleftharpoons} AgHSO_3 \tag{17}$$

$$AgOSO_2^- + O_2 \overset{K_3}{\rightleftharpoons} AgOSO_2^{-1}.O_2 \tag{18}$$

$$AgHSO_3 + O_2 \overset{K_4}{\rightleftharpoons} AgHSO_3.O_2 \tag{19}$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \tag{20}$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \tag{21}$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \tag{22}$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \tag{23}$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \tag{24}$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \tag{25}$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \tag{26}$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \tag{27}$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \tag{28}$$

$$SO_4^{-\bullet} + \text{isoamyl alcohol} \xrightarrow{k_{10}} \text{Non Chain product} \tag{29}$$

By assuming long chain hypothesis and steady state approximation $d[SO_3^{-\bullet}]/dt$, $d[SO_4^{-\bullet}]/dt$, $d[SO_5^{-\bullet}]/dt$, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 30)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[x] + k_8\,[\text{Isoamyl alcohol}]\}\,[SO_4^{-1}] \tag{30}$$

Since the reaction is completely stopped in the presence of [Isoamyl alcohol] at 8 x10^{-4} mol dm^{-3}, so the step (24) and (27) appear to be unimportant.

The step (26) is ignored because the reaction is completely seized in the presence of higher concentration of isoamyl alcohol by omission and substitution from the above mechanism the following rate law can be obtain (31)

$R_{cat} = k_1 [Ag(I)] [S(IV)] / \{k_9[x] + k_{10} [Isoamyl\ alcohol]\}$ (31)

Prasad et al (2013)[22] and Gupta et al (2008)[30] proposed a similar mechanism for the Co_2O_3 and CoO catalysed autoxidation of SO_2 inhibited by formic acid and ethanol respectively, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 1.24×10^4 mol dm^{-3} which is in the range of 10^3 -10^4 and also coincide with the reported value of B of Co_2O_3 catalysed autoxidation of S(IV) by formic acid is 3.58×10^3 mol dm^{-3} So on the basis of calculated value of B we concluded that isoamyl alcohol act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

CONCLUSIONS

The following conclusions are deduced from the results of the isoamyl alcohol inhibited Ag(I) catalysed autoxidation of S(IV) was that inhibit the oxidation with the fast influence. The value of Inhibition factor of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are in the range of 10^3 -10^4 which shows that free radical mechanism is operative.

REFERENCES

1. BERGLUND J., ELDING L J., 1995, Manganese-catalysed autoxidation of dissolved sulphur dioxide in the atmospheric aqueous phase, *Atmospheric Environment*, vol. **29**, No12, pp. 1379-1391.
2. BERGLUND J., FRONAEUS S., ELDING L., 1993, Kinetics and mechanism for manganese catalyzed oxidation of sulfur(IV) by oxygen in aqueous solution, *Inorganic Chemistry,* vol. **32**, No 21, pp. 4527-4537.
3. BRANDT C., VAN ELDIK R., 1995, Transition metal-catalyzed oxidation of sulfur(IV) oxides. Atmospheric-relevant processes and mechanisms, *Chemical Reviews*, vol. **95**, No 1, pp. 119-190.
4. CHEBBI A., CARLIER P., 1996, Carboxylic acids in the troposphere, occurrence, sources, and sinks, a review, *Atmospheric Environment,* vol. **30**, No 24, 4233–4249.143.
5. GRGIC I., DOVZAN A., NOVIC G., HUDNIK V., 1995, Aqueous S(IV) oxidation in the presence of atmospheric aerosol particles, effect of organic ligands on Fe-catalyzed oxidation of S(IV), *Journal of Aerosol Science*, vol. **26**, Suppl. 1, S497-S498.
6. GRGIC I., HUDNIK V., BIZJAK M., LEVEC J., 1991, Aqueous S(IV) oxidation - I. Catalytic effects of some metal ions, *Atmospheric Environment*, vol. **25A**, No 8, pp. 1591-1597.
7. GRGIC I., DOVZAN A., BERCIC G., HUDNIK V., 1998, The effect of atmospheric organic compounds on the Fe-catalyzed S(IV) autoxidation in aqueous solution, *Journal of Atmospheric Chemistry,* vol. **29**, No 1, pp. 315-337.
8. GRGIC I., POZNIC M., 1998, Water soluble fraction of iron and oxalate in atmospheric aerosols and its effect on SO_2 oxidation, *Journal of Aerosol Science,* vol. **29** Suppl. I, S1029-S1030.
9. GRGIC I., PODKRAJSEK B., TURSIC J., 2002, Influence of pH and organics on autoxidation of S(IV) catalysed by manganese; in,

Proceedings from the EUROTRAC-2 Symposium 2002, Transport and Chemical Transformation in the Troposphere, ed. Midgeley, P.M., Reuther, M., Margraf Verlag, Weikersheim.

10. GRGIC I., POZNIC M., BIZJAK M., 1999, S(IV) autoxidation in atmospheric liquid water the role of Fe(II) and the effect of oxalate, *Journal of Atmospheric Chemistry,* vol. **33**, No1, pp. 89-102.
11. KAWAMURA K., KAPLAN I., 1987, Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angels ambient air, *Environmental Science and Technology*, vol. **21**, No 1, pp. 105–110.
12. KAWAMURA K., KASUKABE H., BARRIE L., 1996a, Source and reaction pathways of dicarboxylic acids, keto acids and dicarbonyls in Arctic aerosols, one year of observations, *Atmospheric Environment*, vol. **30**, No 10-11, pp. 1709–1722.
13. LANGNER J., RODHE H., 1991, A global three dimensional model of the tropospheric sulfur cycle, *Journal of Atmospheric Chemistry*, vol. **13**, No 3, pp. 255 – 263.
14. MANOJ S., MISHRA C., SHARMA M., RANI A., JAIN R., BANSAL S., GUPTA K., 2000, Iron, manganese and copper concentrations in wet precipitations and kinetics of the oxidation of SO_2 in rain water at two urban sites, Jaipur and Kota, in Western India, *Atmospheric Environment*, vol. **34**, No. 26, pp. 4479-4486.144.
15. MARTIN L., HILL M., TAI A., GOOD T., 1991, The iron catalyzed oxidation of sulfur(IV) in aqueous solution, Differing effects of organics at high and low pH, *Journal of Geophysical Research*, vol**. 96**, No D2, pp.3085–3097.
16. PASIUK-BRONIKOWSKA, W.,BRONIKOWSKI, T., ULEJCZYK M., 1997, Solubilization of organics in water coupled with sulphite autoxidation, *Water Research,* vol. **31**, No 7, pp. 1767-1775.

17. PODKRAJSEK B., GRGIC I., TURSIC J., BERCIC G., 2006, Influence of atmospheric carboxylic acids on catalytic oxidation of sulfur(IV), *Journal of Atmospheric Chemistry,* vol. **54**, No 2, pp. 103–120.
18. SOUZA S., VASCONCELLOS P., CARVALHO L., 1999, Low molecular weight carboxylic acids in an urban atmosphere, winter measurements in São Paulo City, Brazil, *Atmospheric Environment,* vol. **33**, No 16, pp. 2563–2574.
19. WILKOSZ I., MAINKA A., 2008, Mn(II)-catalysed S(IV) oxidation and its inhibition by acetic acid in acidic aqueous solutions, *Journal of Atmospheric Chemistry,* vol. **60**, No 1-102,pp.1-17.
20. WOLF A., DEUTSCH F., HOFFMANN P., ORTNER H. M., 2000, The influence of oxalate on Fe-catalyzed S(IV) oxidation by oxygen in aqueous solution, *Journal of Atmospheric Chemistry,* vol. **37**, No 2, pp.125-135.
21. ZIAJKA J., PASIUK-BRONIKOWSKA W. 2005, Rate constants for atmospheric trace organics scavenging SO_4^- in the Fe-catalysed autoxidation of S(IV), *Atmospheric Environment,* vol. **39**, No 8, pp.1431-1438.
22. SAMEENA BEGAM, FAIYAZ HUUSAIN, D.S.N. PRASAD, 2013, kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Pelagia research library,***4(1)**, 122-131.
23. BIGELOW, S. L., 1988, Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.
24. ALYEA H. N. AND BACKSTROM, H. L. J., 1929, The inhibitive action of alcohols on the autoxidation of sodium sulfite. *Journal of American Chemical Society,* **51**, 90-107**.**
25. L.G. SILLEN AND A.E. MARTELL, 1964, stability constants of metal ion complex special publication no 17, The chemical soc. Burlington house London.

26. V.F. TOROPOVA I.A. SIROTINA AND V.B. ROTANOVA UCHENYE ZAPISKIK Azanskogo, 1955, Uni. 115 no.353.
27. R. VAN ELDIK, AND G,M. HARRIS, 1980, *Inorg Chem.*, **19**, 880.
28. BACKSTROM H. L. J., 1934, The chain mechanism of the autoxidation of sodium sulfite solutions. *J. Phys. Chem.*(B), **25**, 122-138.
29. CONNICK, R.E., ZHANG, Y.-X., LEE, S., ADAMIC, R., CHIENG, P.,1995, Kinetics and mechanism of the oxidation of HSO_3 by O_2, the uncatalyzed reaction. *Inorganic Chemistry*, **34**,4543–4553.
30. GUPTA K.S., MEHTA R.K., SHARMA A.K., MUDGAL P.K., BANSAL S.P., 2008, Kinetics of the uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 Catalyzed autoxidation of Sulfur(IV) in alkaline medium, *Transition Metal Chemistry*, **33**, 809-817.

CHAPTER - VI

Kinetics of Sodium Benzoate Inhibited Uncatalysed and Ag (I) Catalysed Autoxidation of S (IV) in Acidic Medium

ABSTRACT

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. Based on the observed results a free radical mechanism operative and following rate law has been proposed.

$-d\,[S(IV)/dt \quad = \quad (k_1+k_2[Ag])\,[S(IV)]/\,1 + \; B\,[\text{Sodium benzoate}]$

INTRODUCTION

Petroleum hydrocarbons are one of the major pollutants that enter both aquatic and atmospheric systems via oil spills, oil fires, crude oil refining and motor exhaust fumes (Yiwei Deng, 2006)[22]. Upon the emission of petroleum hydrocarbons into the environment, immediate changes in their chemical and physical properties occur as a result of simultaneous chemical and physical processes including photo degradation evaporation, dispersion and emulsification (Galt et al., 1991[8], Payne and Phillips, 1985[15]). The photo degradation of petroleum hydro carbons plays a critical role in determining their fate in the environment as a wide variety of photo degradation products such as aromatic/aliphatic acids, alcohols and aldehydes have been identified (Payne and Phillips 1985[15], Hansen 1975[12]). The primary photo degradation products are carboxylic acids with significant levels of benzoic acid and its sodium salt that is presumably formed from the decomposition of alkyl-substituted benzenes (Hansen, 1975[12]). Aromatic acids (AAs, e.g., BA and salicylic acids) have been detected in the fumes of automobiles, heavy duty diesel trucks, industrial boilers burning distillate fuel oil and tar pots heating asphalt (Rogge et al., 1993[18], 1997[19]). Several recent studies have shown that the interaction between AAs (e.g., BA) and sulfuric acid in the atmosphere promotes efficient formation of organic and sulfate aerosols in the polluted atmosphere (Zhang et al., 2004).[23,24] These aerosols are associated largely with acid rain and photochemical smog, which affect human health, and in part are responsible for reduction in visibility of urban atmosphere. Thus it is important to study the transformation and fate of AAs in order to understand several critical atmospheric processes associated with atmospheric aerosols. Several studies have reported on the Fe(III)- catalyzed photodecomposition of BA and other organic acids in surface water or wastewater treatment systems (Bates and Uri 1953[4], Cunninghamet al., 1988[7], Goldberg et al. 1993[9], Andreozziand Marotta 2004[2]). However, most of the previous experiments have been performed with highly acidic (pH=2) solutions, or containing high concentrations (41mM) of BA or Fe(III) or particular iron oxides. Little information exists on the intermediate products, degradation mechanisms and wavelength dependence of the degradation. The purpose of the present work was to study the influence of sodium benzoate on the Ag(I) catalysed S(IV) oxidation under the conditions representative for acidic medium.

EXPERIMENTAL

The experimental procedure was exactly the same as described earlier.[20] All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature $30\underline{+}1^0$ C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at $1600\underline{+}10$ rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically. The reproducibility of replicate measurements was generally better than $10\underline{+}1$ %. All calculations were performed in MS Excel.

PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S(VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure.

The product analysis showed the recovery of sulphate to be 98±1%. in all cases in agreement with eq. (1)

$$S(IV) + 0.5\ O_2 \longrightarrow S(VI) \qquad (1)$$

RESULTS

Preliminary Investigation-

The kinetics of both uncatalysed, Ag (I) Catalysed and sodium benzoate inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30^o C. In both the cases the first order dependence of S(IV) was observed in the kinetics data treatment for the determination of first order rate constant $k_1$was carried out from log [S(IV)] versus time, t. The plots were shown in fig 6.1. From the fig.6.1 observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by sodium benzoate.

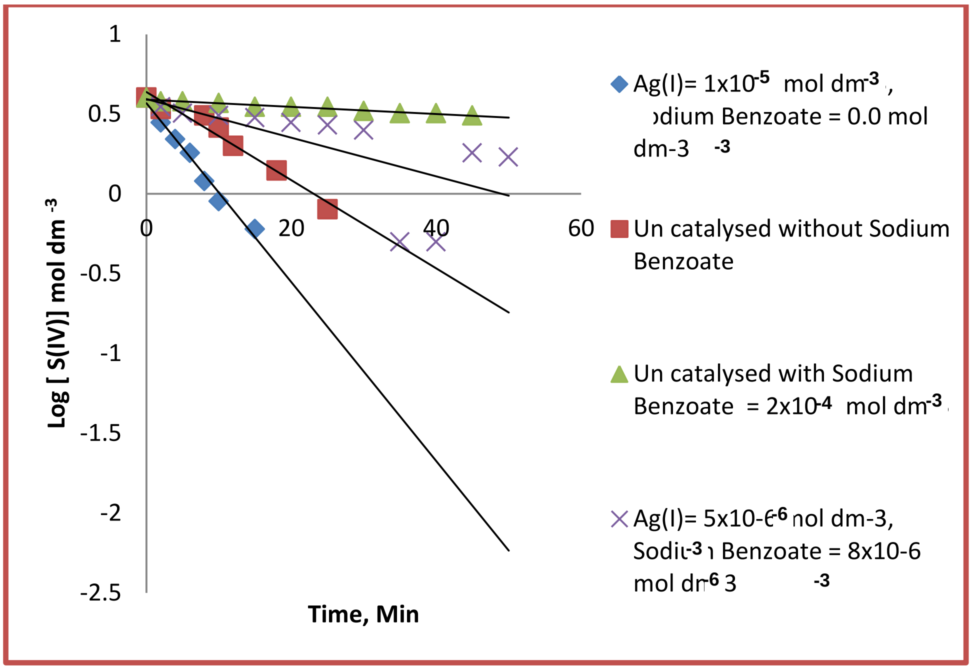


Fig.6.1 : The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2x 10^{-3} mol dm^{-3} at pH = 4.95, t = 30^{o} C.

(◇) Ag (I) = 1x 10^{-5} mol dm^{-3}, [Sodium benzoate] = 0.0 mol dm^{-3}

(□) Uncatalysed without sodium benzoate

(△) Uncatalysed with [Sodium benzoate] = $2x10^{-4}$ mol dm^{-3}

(x) Ag (I) = 5x 10^{-6} mol dm^{-3}, [Sodium benzoate] = 8x 10^{-6} mol dm^{-3}

Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of Ag(I) and all the solutions were prepared in doubly distilled water.

Table- 6.1

Quantitative Analysis of Sulphate in Final Product Solution

10^3 [S(IV)] mol dm^{-3}	Ag (I) mol dm^{-3}	pH	10^3 [SO_4^{-2}] mol dm^{-3}	[SO_4^{-2}] /[S(IV)]	% of S(IV) recovery
5.0	0.00	4.95	4.90	0.980	98.0
5.0	5x10^{-6}	4.95	4.92	0.984	98.4
5.0	1x10^{-5}	4.95	4.95	0.990	99.0

Table- 6.2

Variation of [S (IV)] at pH = 4.95, t = 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	3	4
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot			
(0)	0.0	0.0	0.0	0.0
(2)	0.5	0.6	1.3	1.6
(8)	0.8	0.9	2.1	2.2
(10)	1.0	1.4	3.2	3.2
(12)	1.2	2.0	3.8	4.3
(18)	1.4	2.6	4.6	5.4
(25)	1.6	3.2	4.8	6.5
∞	2.0	4.0	6.0	8.0
(10^3) k_1 s^{-1}	**1.04**	**1.06**	**1.09**	**1.09**

Figures in parentheses denote time in minutes.

Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range $1x10^{-3}$ mol dm^{-3} to $4x10^{-3}$ mol dm^{-3} at pH = 4.95, t = 30^o C in acetate buffered medium. The kinetics was found to be first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of first order rate constant k_1 are given in table - 6.3. The dependence of reaction rate on [S(IV)] follows the rate law (2)

$$-d [S(IV)] /dt = k_1 [S(IV)] \qquad (2)$$

Table- 6.3

The values of k_1 for uncatalysed reaction at different [S(IV)], pH = 4.95, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	**(10^{3}) k_1 s^{-1}**
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

[Sodium benzoate] Dependence

The major aim of this study was to examine the effect of sodium benzoate on the autoxidation of S(IV) in acetate buffer medium and varying the [Sodium benzoate] from $8x10^{-8}$ mol dm^{-3} to $2x10^{-4}$ mol dm^{-3}, we observed the rate of the reaction decreased by increasing [Sodium benzoate]. The results are given in table 6.4 However the nature of the [S(IV)] dependence in presence of sodium benzoate did not change and remains first order. The first order rate constant k_{inh}, in the presence of sodium benzoate was defined by rate law (3)

$$-d\,[S(IV)]\,/dt \quad = \quad k_{inh}\,[S(IV)] \qquad (3)$$

The values of k_{inh} in the presence of sodium benzoate decreased with increasing [Sodium benzoate] are given in table 6.5 which are in agreement with the rate law (4)

$$k_{inh} = k_1 / (1+B\,[\text{Sodium benzoate}]) \qquad (4)$$

Where B is inhibition parameter for rate inhibition by sodium benzoate

The equation (4) on rearrangement becomes

$$1/\,k_{inh} = 1/\,k_1 + B\,[\text{Sodium benzoate}]\,/\,k_1 \qquad (5)$$

In accordance with the equation (5) the plot of 1/ k_{inh} v/s [Sodium benzoate] was found to be linear with non- zero intercept fig 6.2 The values of intercept (1/ k_1) and slope (B/ k_1) were found to be 1.29×10^3 s and 4.76×10^6 mol dm^{-3} s at pH = 4.95, t = 30^o C. From these values the value of inhibition parameter B was found to be 3.68×10^4 mol dm^{-3}

Table- 6.4

Variation of [Sodium Benzoate], at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[Sodium Benzoate] mol dm^{-3}	**$8x10^{-8}$**	**$3x10^{-7}$**	**$5x10^{-7}$**	**$8x10^{-7}$**	**$2x10^{-6}$**	**$6x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$8x10^{-5}$**	**$2x10^{-4}$**
Time, (Min)	Volume of 5 x10^{-3}mol dm^{-3} Hypo for 5 ml aliquot									
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.5	0.4	0.5	0.4	0.4	0.4	0.2	0.1	0.2
(5)	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.5	0.5	0.2
(10)	1.4	1.2	1.3	1.2	1.2	1.0	1.0	1.0	0.8	0.3
(15)	1.8	1.6	1.7	1.6	1.6	1.4	1.4	1.2	1.0	0.5
(20)	2.1	2.1	2.3	1.9	2.0	1.7	1.7	1.7	1.2	0.5
(25)	2.6	2.5	2.6	2.4	2.2	2.0	2.0	1.9	1.4	0.5
(30)	3.0	3.0	3.0	2.7	2.5	2.3	2.2	2.0	1.6	0.7
(35)	3.3	3.2	3.2	3.0	2.6	2.6	2.4	2.1	1.8	0.8
(40)	3.6	3.4	3.2	3.2	3.0	2.9	2.6	2.2	2.0	0.8
(45)	3.7	3.7	3.4	3.3	3.2	3.0	2.8	2.3	2.0	0.9
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	0.2
(10^{3}) k_1 s^{-1}	**0.919**	**0.863**	**0.714**	**0.647**	**0.553**	**0.505**	**0.426**	**0.326**	**0.276**	**0.086**

Figures in parentheses denotes time in minute.

Table- 6.5

The values of k_{inh} at different [Sodium benzoate] at pH = 4.95, t = 30° C

$CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH= 3x10^{-2}$ mol L^{-1}

[Sodium benzoate] mol dm^{-3}	$10^3\ k_{inh}\ s^{-1}$	$1/k_{inh}$ s
$8.0x10^{-8}$	0.919	1088
$3.0x10^{-7}$	0.863	1159
$5.0x10^{-7}$	0.714	1401
$8.0x10^{-7}$	0.647	1546
$2.0x10^{-6}$	0.553	1808
$6.0x10^{-6}$	0.505	1980
$8.0x10^{-6}$	0.426	2347
$5.0x10^{-5}$	0.326	3067
$8.0x10^{-5}$	0.276	3623
$2.0x10^{-4}$	0.086	11628

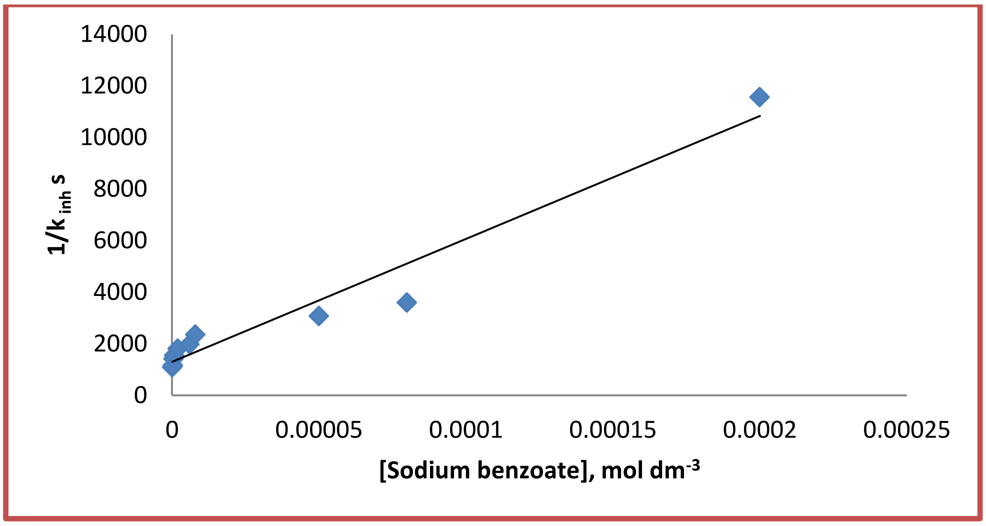


Fig.6.2 : Effect of sodium benzoate at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30° C in acetate buffered medium.

Ag(I) Catalysed Reaction

At first the kinetics of Ag(I) Catalysed reaction in the absence of inhibitor was studied.

[S(IV)] Variation

The dependence of S (IV) on reaction rate was studied by varying [S(IV)] from $1x10^{-3}$ mol dm^{-3} to $10x10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5x10^{-6}$ mol dm^{-3} and $1x10^{-5}$ mol dm^{-3} at pH = 4.95, t = 30^o C. The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in fig 6.1

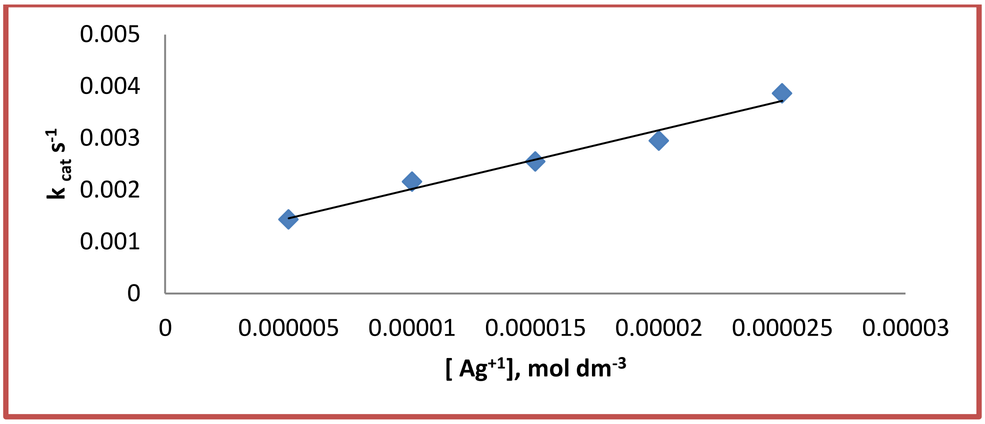
Ag(I) Variations

The dependence of Ag(I) on the reaction rate was studied by varying Ag (I) from $5x10^{-6}$ mol dm^{-3} to $2.5x10^{-5}$ mol dm^{-3} at S(IV) = $2x10^{-3}$ mol dm^{-3} pH = 4.95, t = 30^o C in acetate buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig. 6.3. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law – (6)

$$-d\,[S(IV)]\,/dt = k_{cat}\,[S(IV)] = (k_1+k_2[Ag(I)]\,[S(IV)] \qquad (6)$$

$$\text{Or } k_{cat} = k_1+k[Ag(I)] \qquad (7)$$

From the plot in fig 6.3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be $0.72x\ 10^1$ s and $8.6\ x\ 10^{-3}$ mol dm^{-3} respectively at pH = 4.95, t = 30^o C in acetate buffered medium.



<u>Fig. 6.3</u> : The dependence of catalyst concentration at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^o C in acetate buffered medium.

Table- 6.6

Variation of [S(IV)] = $2x10^{-3}$ mol dm^{-3} at Ag (I) =$5x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.8	1.5	2.0	2.2
(4)	0.4	1.0	1.7	2.4	3.3	4.5
(6)	0.6	1.2	2.7	3.0	4.5	6.5
(8)	0.9	1.5	3.6	4.0	7.0	9.8
(10)	1.2	1.7	5.0	5.5	9.3	12.1
(15)	1.4	3.0	5.5	9.0	11.5	14.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.43**	**1.42**	**1.41**	**1.44**	**1.46**	**1.50**

Figures in parentheses denotes time in minutes

Table- 6.7

Variation of [S(IV)] = 2×10^{-3} mol dm^{-3} at Ag (I) =1×10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH= 3×10^{-2} mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.9	3.0	4.5	5.6
(4)	0.8	1.8	2.8	4.8	6.3	7.8
(6)	1.2	2.2	3.6	5.9	7.8	9.5
(8)	1.4	2.8	4.5	7.8	8.9	10.2
(10)	1.5	3.1	5.0	8.9	12.5	12.8
(15)	1.7	3.4	7.0	10.3	13.6	17.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**2.19**	**2.15**	**2.15**	**2.18**	**2.14**	**2.10**

Figures in parentheses denotes time in minutes.

Table- 6.8

Variation of Ag (I) at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5x10^{-6}$**	**$1x10^{-5}$**	**$1.5x10^{-5}$**	**$2x10^{-5}$**	**$2.5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.4	2.5	2.4
(4)	1.0	1.8	1.8	2.7	2.5
(6)	1.2	2.2	2.0	2.9	3.0
(8)	1.5	2.8	2.2	3.7	3.5
(10)	1.7	3.1	3.4		
(15)	3.0	3.4			
∞	4.0	4.0	4.0	4.0	4.0
$(10^{3})k_1$ s^{-1}	**1.42**	**2.15**	**2.54**	**2.94**	**3.88**

Figures in parentheses denotes time in minutes

Table - 6.9

The values of k_{cat} at different concentration of Ag (I) mol dm^{-3}, pH = 4.95, t = 30° C, $CH_3COONa = 7x10^{-2}$ mol L^{-1} $CH_3COOH = 3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	$10^3\ k_{cat}$ s^{-1}
0.000005	1.42
0.00001	2.15
0.00015	2.54
0.00020	2.94
0.00025	3.88

Variation of pH

Variation of pH was carried out from 4.02 - 5.25 at different [S(IV), Ag (I), [Sodium benzoate] and temperatures. The rate decreases slightly by varying pH is inverse H^+ ion dependence was observed. From the plot of log k_1 v/s log (H^+) the order with respect to H^+ is 0.21 which is a fractional order and can be neglected as shown in fig 6.4.

Table - 6.10

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Sodium benzoate] =$8.0x10^{-6}$ mol dm^{-3}, t=30° C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}

pH	10^3 k s^{-1}
4.02	0.354
4.35	0.392
4.56	0.484
4.75	0.659
4.95	0.853
5.25	0.926

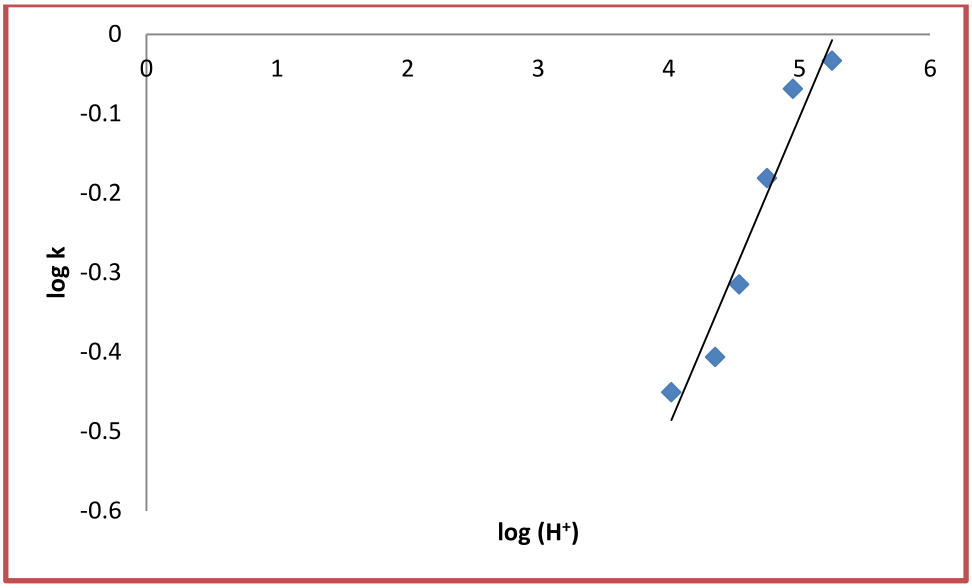


Fig. 6.4 : Effect of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Sodium benzoate]= 8.0x10^{-6} mol dm^{-3}, t= 30° C in acetate buffered medium.

Table - 6.11

Rate of Ag (I) Catalysed Autoxidation in the Presence of Sodium Benzoate.

[Sodium benzoate], mol dm^{-3}	Ag (I) =5x10^{-6} mol dm^{-3}	Ag (I) =1 x 10^{-5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.02			
8.0 x 10^{-6}	0.354 x 10^{-3}	0.484 x 10^{-3}	0.926 x 10^{-3}
5.0x 10^{-5}	0.266 x 10^{-3}	_	_
2.0 x 10^{-4}	0.183 x 10^{-3}	_	_
pH = 4.50			
8.0 x 10^{-6}	0.535 x 10^{-3}	0.658 x 10^{-3}	1.33 x 10^{-3}
5.0x 10^{-5}	0.318 x 10^{-3}	_	_
2.0 x 10^{-4}	0.301 x 10^{-3}	_	_
pH = 5.25			
8.0 x 10^{-6}	0.626 x 10^{-3}	0.955x 10^{-3}	1.42 x 10^{-3}
5.0 x 10^{-5}	0.509 x 10^{-3}	_	_
2.0 x 10^{-4}	0.468 x 10^{-3}	_	_

Table - 6.12

Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of sodium benzoate.

[Sodium benzoate] 8.0 x 10^{-6} mol dm^{-3}	Ag (I) =5x10^{-6} mol dm^{-3}	Ag (I) =1 x10^{-5} mol dm^{-3}	Ag (I) =1.5x10^{-5} mol dm^{-3}
pH = 4.50			
	4.01	**4.44**	**2.74**

Table - 6.13

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Sodium Benzoate] = 8x10^{-6} mol dm^{-3}, t= 30° C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.6	0.8	0.5	0.8
(5)	0.8	0.8	0.9	1.3	1.5	1.4
(10)	1.0	1.0	1.1	1.6	1.8	1.8
(15)	1.3	1.2	1.4	2.2	2.2	2.4
(20)	1.4	1.5	1.6	2.8	2.8	2.8
(25)	1.7	1.7	2.2	3.0	3.0	3.3
(30)	2.0	2.0	2.4	3.2	3.3	3.4
(35)	2.3	2.2	2.6	3.3	3.5	3.5
(40)	2.5	2.4	2.8	3.3	3.5	3.6
(45)	2.6	2.6	3.0	3.4	3.6	3.6
(50)	2.6	3.0	3.1	3.4	3.7	3.8
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.354**	**0.392**	**0.484**	**0.659**	**0.853**	**0.926**

Figures in parentheses denotes time in minutes

Table - 6.14

Variation of pH at [S(IV)] = 4×10^{-3} mol dm^{-3}, Ag (I) = 5×10^{-6} mol dm^{3}, [Sodium Benzoate] = 8×10^{-6} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1	1.1	1.5	1.7	1.8	2.2
(5)	1.7	1.6	2.1	2.4	2.5	2.8
(10)	2.4	2.2	2.6	2.8	3.2	3.2
(15)	3.2	2.6	3.3	3.4	3.6	3.7
(20)	3.4	3.0	3.7	4.2	4.2	3.9
(25)	4	3.2	4.5	4.7	4.8	4.7
(30)	4.4	3.4	5.1	5.5	5.5	5.6
(35)	4.9	4.0	5.5	5.9	6.2	6.5
(40)	5.2	4.2	5.7	6.0	7.0	7.3
(45)	5.3	4.5	6.2	6.4	7.3	7.6
(50)	5.4	6.8	6.3	7.3	7.5	2.2
∞	8.0	8.0	8.0	8.0	8.0	8.0
(10^3) k_1, s^{-1}	**0.372**	**0.406**	**0.498**	**0.653**	**0.864**	**0.929**

Figures in parentheses denotes time in minutes

Table - 6.15

Variation of pH at [S(IV)] = 6x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Sodium Benzoate] = 8x10^{-6} mol dm^{-3}, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.9	2.1	2.3	2.3	3.2	3.3
(5)	2.6	2.8	3.2	3.3	4.5	4.6
(10)	3.3	3.4	3.6	4.2	5.1	5.5
(15)	4.3	4.6	4.7	5.0	6.2	6.6
(20)	4.9	5.8	5.5	5.9	7.5	7.8
(25)	5.3	6.2	6.4	7.2	8.8	9.0
(30)	5.7	7.0	7.0	8.2	9.6	9.6
(35)	6.0	7.5	7.3	8.5	10.5	10.5
(40)	6.4	8.2	7.9	9.0	10.6	10.8
(45)	7.3	8.3	8.4	9.5	10.9	11.2
(50)	9.2	8.5	10.2	11.0		
∞	12.0	12.0	12.0	12.0	12.0	12.0
(10^3) k_1, s^{-1}	**0.355**	**0.403**	**0.482**	**0.653**	**0.864**	**0.929**

Figures in parentheses denotes time in minutes

Table - 6.16

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $1x10^{-5}$ mol dm^{-3}, [Sodium benzoate] = $8x10^{-6}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.5	0.6	0.8	0.8	0.8
(5)	0.8	0.9	0.9	1.3	1.3	1.0
(10)	1.2	1.3	1.2	1.6	1.7	1.5
(15)	1.4	1.5	1.4	2.2	2.2	1.9
(20)	1.6	1.9	1.7	2.8	2.4	2.4
(25)	1.9	2.2	2.2	3.0	3.1	2.9
(30)	2.2	2.5	2.5	3.1	3.2	3.4
(35)	2.6	2.9	2.9	3.2	3.5	3.7
(40)	3.2	3.2	3.4	3.2	3.8	3.9
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.535**	**0.601**	**0.658**	**0.705**	**1.07**	**1.33**

Figures in parentheses denotes time in minutes

Table 6.17

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 1.5x10^{-5} mol dm^{-3}, [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.9	0.9	1.0	0.8	0.8
(5)	1.0	1.4	1.5	1.5	1.4	1.4
(10)	1.2	1.9	1.9	2.0	1.9	1.9
(15)	1.4	2.5	2.3	2.4	2.4	2.5
(20)	1.6	2.9	2.9	2.8	2.9	3.0
(25)	2.2	3.0	3.2	3.1	3.3	3.3
(30)	2.4	3.0	3.3	3.5	3.7	3.8
(35)	3.3					
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.626**	**0.798**	**0.955**	**1.010**	**1.27**	**1.42**

Figures in parentheses denotes time in minutes

Table - 6.18

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Sodium benzoate] = $5x10^{-5}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.6	0.8	0.5	0.8
(5)	0.7	0.7	0.9	1.3	0.8	1.0
(10)	0.9	1.0	1.1	1.5	1.0	1.3
(15)	1.1	1.2	1.4	1.7	1.3	1.5
(20)	1.2	1.4	1.6	2.0	1.6	1.9
(25)	1.3	1.5	1.8	2.3	2.0	2.0
(30)	1.5	1.9	2.0	2.4	2.3	2.2
(35)	1.8	2.0	2.1	2.6	2.5	2.4
(40)	2.0	2.2	2.3	2.9	2.7	2.6
(45)	2.2	2.3	2.5	3.0	3.0	2.9
(50)	2.4	2.4	2.6	3.0	3.0	3.5
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.266**	**0.290**	**0.318**	**0.440**	**0.465**	**0.509**

Figures in parentheses denotes time in minutes

Table - 6.19

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3} Ag (I) = 5×10^{-6} mol dm^{-3}, [Sodium Benzoate] = 2×10^{-4} mol dm^{-3}, t = 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.8	0.8	0.8	0.8
(5)	0.6	0.7	0.9	0.9	1.0	1.0
(10)	0.8	0.8	1.2	1.0	1.3	1.3
(15)	0.9	0.9	1.4	1.2	1.6	1.5
(20)	1.0	1.0	1.7	1.3	1.8	1.9
(25)	1.2	1.2	2.0	1.5	2.0	2.0
(30)	1.4	1.4	2.2	1.6	2.3	2.2
(35)	1.7	1.5	2.4	1.8	2.5	2.4
(40)	1.8	1.8	2.6	2.2	2.7	2.6
(50)	1.8	2.0	2.6	2.5	3.2	2.9
(60)	2.0	2.2	2.6	3.1	3.2	3.5
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.183**	**0.202**	**0.301**	**0.331**	**0.441**	**0.468**

Figures in parentheses denotes time in minutes

Table - 6.20

Variation of pH at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = $5\text{x}10^{-6}$ mol dm^{-3}, [Sodium Benzoate] = $8\text{x}10^{-6}$ mol dm^{-3}, t= 35^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.7	0.8	0.9	0.9	0.8
(5)	0.9	0.9	1.2	1.3	1.5	1.2
(10)	1.3	1.3	1.4	1.6	1.8	1.7
(15)	1.5	1.9	1.9	2.2	2.2	2.3
(20)	1.6	2.3	2.2	2.8	2.8	2.6
(25)	1.9	2.6	2.3	3.1	3.1	3.0
(30)	2.2	2.9	2.6	3.2	3.3	3.3
(35)	2.6	3.0	3.2	3.3	3.5	3.5
(40)	2.6	3.0	3.4	3.4	3.5	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.414**	**0.61**	**0.689**	**0.799**	**0.887**	**0.943**

Figures in parentheses denotes time in minutes

Table - 6.21

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Sodium Benzoate] = 8x10^{-6} mol dm^{-3}, t= 40° C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.7	0.8	0.9	0.9	0.8
(5)	0.9	1.0	1.4	1.4	1.5	1.2
(10)	1.3	1.4	1.9	1.9	1.8	1.7
(15)	1.5	2.0	2.2	2.4	2.3	2.3
(20)	1.9	2.2	2.4	2.9	2.8	2.6
(25)	2.3	2.6	2.9	3.0	3.2	3.3
(30)	2.5	2.9	3.1	3.2	3.3	3.4
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.504**	**0.669**	**0.763**	**0.869**	**0.947**	**1.03**

Figures in parentheses denotes time in minutes

Table- 6.22

Variation of [S(IV)] at Ag (I) = 5 x10^{-6} mol dm^{-3} , [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	1.8	3.2	3.4	3.6
(5)	0.6	1.5	2.5	4.5	4.6	4.8
(10)	0.8	1.8	3.2	5.1	5.5	6.4
(15)	0.9	2.2	3.6	6.2	6.9	8.2
(20)	1.0	2.8	4.2	7.5	8.2	9.5
(25)	1.1	3.0	4.8	8.8	10.5	10.2
(30)	1.2	3.3	5.5	9.6	12.3	12.3
(35)	1.5	3.5	6.2	10.5	12.9	13.4
(40)	1.7	3.5	7.0	10.6	13.6	14.5
(45)	1.8	3.6	7.3	10.9	14.5	16.8
(50)	1.9	3.7	7.5	3.2	15.2	19.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**0.831**	**0.853**	**0.849**	**0.864**	**0.890**	**0.809**

Figures in parentheses denotes time in minutes

Table- 6.23

Variation of [S(IV)] at Ag (I) =1x10^{-5} mol dm^{-3}, [Sodium benzoate] = 8x10^{6} mol dm^{-3}, pH = 4.95, t = 30^{o}C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.8	1.8	3.2	3.4	3.6
(5)	0.8	1.3	2.8	4.6	4.6	4.8
(10)	1.0	1.7	3.6	5.5	5.8	6.4
(15)	1.2	2.2	4.9	6.6	7.1	8.2
(20)	1.3	2.4	5.8	7.8	8.5	9.8
(25)	1.5	3.1	6.5	8.8	10.5	10.5
(30)	1.6	3.2	7.0	9.6	12.3	12.3
(35)	1.8	3.5	7.3	10.2	13.2	13.4
(40)	1.9	3.8	7.4	11.0	14.1	14.5
(45)			7.4	11.5	15.2	17.9
(50)					19.4	19.8
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**1.06**	**1.07**	**1.02**	**1.01**	**1.02**	**1.00**

Figures in parentheses denotes time in minutes

Table- 6.24

Variation of [S(IV)] at Ag (I) =2 x10^{-5} mol dm^{-3}, [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.8	1.9	3.3	3.4	3.6
(5)	0.8	1.4	2.8	4.6	4.8	6.3
(10)	1.2	1.9	3.8	5.6	6.2	8.6
(15)	1.4	2.4	4.7	6.8	7.6	10.2
(20)	1.6	2.9	5.8	7.9	8.8	13.4
(25)	1.7	3.3	6.8	8.8	12.4	15.5
(30)	1.8	3.7	7.2	9.6	14.5	17.5
(35)			7.5	11.3	15.0	18.9
(40)				11.6		
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.22**	**1.27**	**1.26**	**1.23**	**1.23**	**1.27**

Figures in parentheses denotes time in minutes

Table- 6.25

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.5	0.6	0.7
(5)	0.6	0.8	0.8	0.9	1
(10)	0.8	1.0	1.2	1.2	1.3
(15)	0.9	1.2	1.4	1.4	1.5
(20)	1.0	1.3	1.6	1.6	1.7
(25)	1.1	1.5	1.7	1.6	1.7
(30)	1.2	1.6	1.8	1.9	1.8
(35)	1.5	1.8			
(40)	1.7	1.9			
(45)	1.8				
(50)	1.9				
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.831**	**1.06**	**1.22**	**1.35**	**1.42**

Figures in parentheses denotes time in minutes

Table- 6.26

Variation of Ag (I) at S(IV)]= 2 x10^{-3} mol dm^{-3}, [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.8	0.8	0.9	1.0
(5)	1.5	1.3	1.4	1.5	1.6
(10)	1.8	1.7	1.9	2.0	2.0
(15)	2.2	2.2	2.4	2.4	2.4
(20)	2.8	2.4	2.9	2.9	3.3
(25)	3	3.1	3.3	3.5	3.6
(30)	3.3	3.2	3.7	3.7	
(35)	3.5	3.5			
(40)	3.5	3.8			
(45)	3.6				
(50)	3.7				
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.853**	**1.07**	**1.27**	**1.33**	**1.41**

Figures in parentheses denotes time in minutes

Table- 6.27

Variation of Ag (I) at S(IV)]= 4 x10^{-3} mol dm^{-3} [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	1.8	1.8	1.9	3.8	3.8
(5)	2.5	2.8	2.8	4.8	4.7
(10)	3.2	3.6	3.8	5.8	5.9
(15)	3.6	4.9	4.7	6.8	6.7
(20)	4.2	5.8	5.8	7.0	7.0
(25)	4.8	6.5	6.8	7.4	7.2
(30)	5.5	7.0	7.2		
(35)	6.2	7.3	7.5		
(40)	7.0	7.4			
(45)	7.3	7.4			
(50)	7.6				
∞	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1 s^{-1}	**0.880**	**1.02**	**1.26**	**1.34**	**1.43**

Figures in parentheses denotes time in minutes

Table- 6.28

Variation of sodium benzoate at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) =5 $x10^{-6}$ mol dm^{-3}, pH = 4.95, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Sodium benzoate] mol dm^{-3}	**$3x10^{-7}$**	**$5x10^{-7}$**	**$8x10^{-7}$**	**$2x10^{-6}$**	**$6x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$8x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(5)	1.5	1.5	1.5	1.5	1.5	1.5	0.8	0.8
(10)	2.2	1.8	1.8	1.8	1.8	1.8	1.0	0.9
(15)	2.5	2.2	2.2	2.2	2.2	2.2	1.3	1.0
(20)	3.0	2.8	2.8	2.8	2.8	2.8	1.6	1.2
(25)	3.2	3.0	3.2	3.0	3.0	3.0	1.8	1.3
(30)	3.7	3.5	3.3	3.3	3.3	3.3	2.0	1.5
(35)	3.8	3.8	3.5	3.5	3.5	3.5	2.2	1.8
(40)					3.5	3.5	2.4	2.0
(45)						3.6	2.6	2.2
(50)						3.7	2.7	2.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.07**	**1.00**	**0.972**	**0.945**	**0.898**	**0.853**	**0.534**	**0.468**

Figures in parentheses denotes time in minutes

Table- 6.29

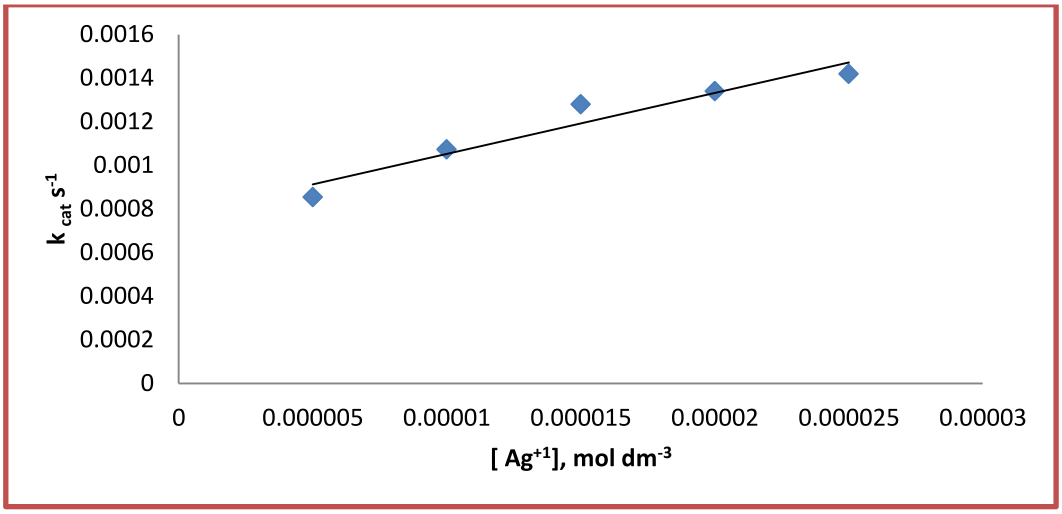
Variation of sodium benzoate at [S(IV)]= $2x10^{-3}$ mol dm^{-3}, Ag (I) = $1x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Sodium benzoate] mol dm^{-3}	**$3x10^{-7}$**	**$5x10^{-7}$**	**$8x10^{-7}$**	**$2x10^{-6}$**	**$6x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$8x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(5)	1.5	1.5	1.5	1.5	1.5	1.5	0.8	0.8
(10)	2.2	1.8	1.8	1.8	1.8	1.8	1.0	0.9
(15)	2.5	2.2	2.2	2.2	2.2	2.2	1.3	1.0
(20)	3.0	3.0	2.8	3.0	2.8	2.8	1.6	1.2
(25)	3.5	3.2	3.4	3.1	3.2	3.0	1.8	1.3
(30)	3.7	3.6	3.4	3.3	3.4	3.3	2.0	1.5
(35)					3.6	3.5	2.2	1.8
(40)					3.4	3.5	2.4	2.3
(45)							2.8	2.5
(50)							3.1	2.7
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.30**	**1.17**	**1.08**	**0.969**	**0.929**	**0.898**	**0.603**	**0.526**

Figures in parentheses denotes time in minutes

[Sodium benzoate] Dependence

To know the effect of sodium benzoate on Ag (I) catalysed autoxidation of S(IV) sodium benzoate variation was carried out from 3x10^{-7} mol dm^{-3} to 8 x 10^{-5} mol dm^{-3} at two different Ag (I) that is 5x10^{-6} mol dm^{-3} to 1.0 x 10^{-5} mol dm^{-3} but fixed S (IV) = 2x10^{-3} mol dm^{-3} at pH= 4.95 and t=30^o C. The results indicated that by increasing sodium benzoate the rate becomes decelerates.



<u>Fig.6.4</u> : Effect of catalyst at [S(IV)] = 2x10^{-3} mol dm^{-3}, [Sodium benzoate] = 8.0x10^{-6} mol dm^{-3}, t= 30^o C in acetate buffered medium. The value of intercept and slope are 7.7 x 10^{-4} s and 2.7 x 10^{1} mol dm^{-3} s respectively. Depending on the observed results the reaction follows the following rate law (8)

-d [S(IV)] /dt = $(k_1+k_2[Ag(I)]$ [S(IV)] / 1 + B [Sodium benzoate] (8)

Where k_{inh} = $(k_1+k_2[Ag(I)]$ / 1 + B [Sodium benzoate] = k_{cat} / 1 + B [Sodium benzoate] (9)

1/ k_{inh} = 1 + B [Sodium benzoate] / k_{cat} (10)

1/ k_{inh} = 1/ k_{cat} + B [Sodium benzoate] / k_{cat} (11)

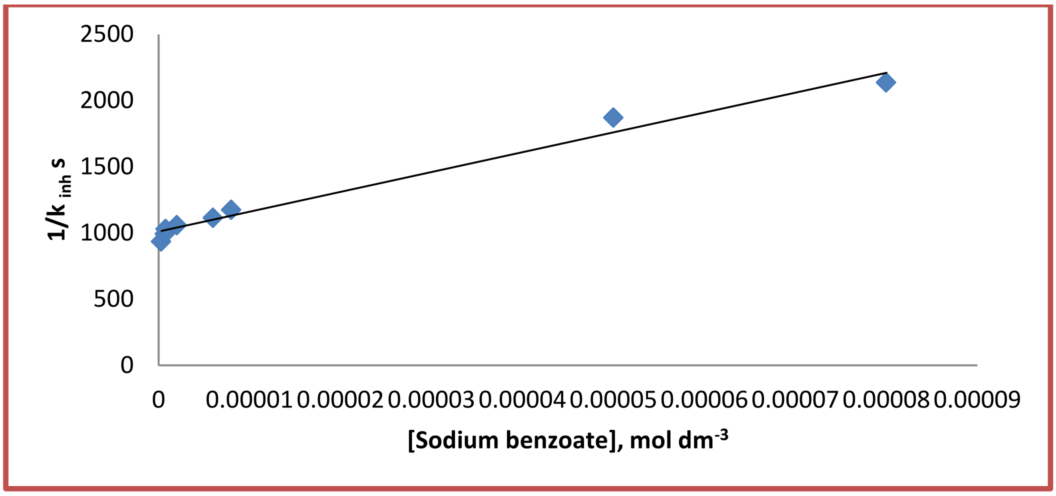


Fig.6.5 : Effect of sodium benzoate at [S(IV)] = 2x10^{-3} mol dm^{-3} Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium. The Plot of 1/ k_{inh} v/s [Sodium benzoate] is linear with intercept 1.01 x 10^{3} s and slope 1.49 x 10^{7} mol dm^{-3} s from which the value of B = 1.48 x 10^{4} mol dm^{-3}

Table- 6.30

The values of k_{inh} at different [Sodium benzoate], [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C CH_3COONa = 7x10^{-2} mol L^{-1} CH_3OOH = 3x10^{-2}mol L^{-1}

[Sodium benzoate] mol dm^{-3}	10^{3} k_{inh} s^{-1}	1/k_{inh} s
3.0x10^{-7}	1.07	935
5.0x10^{-7}	1.00	1000
8.0x10^{-7}	0.972	1029
2.0x10^{-6}	0.945	1058
6.0x10 $^{-6}$	0.898	1114
8.0x10^{-6}	0.853	1172
5.0x10^{-5}	0.534	1873
8.0x10^{-5}	0.468	2137

Effect of Temperature

The values of k_{obs} were determined at three different temperatures in the range of 30^o C to 40^o C. The results are given in table 6.31 by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 24.11 KJ mol^{-1}

Table – 6.31

Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3}, [Sodium benzoate] = 8.0 x 10^{-6}mol dm^{-3} pH = 4.95

t^o C	$10^3 k_{obs} s^{-1}$
30	0.853
35	0.949
40	1.10

Table- 6.32

Variation of [S(IV)] at Ag (I) =1x10^{-5} mol dm^{-3}, [Sodium benzoate] =8x10^{-6} mol dm^{-3}, pH = 4.95, t = 35^o C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.6	1.9	3.3	3.5	3.7
(5)	0.8	0.8	2.6	4.6	4.8	4.9
(10)	1.0	1.2	3.4	5.3	5.6	6.5
(15)	1.2	1.9	4.3	6.4	7.1	8.5
(20)	1.3	2.5	5.2	7.4	8.5	9.5
(25)	1.4	2.9	6.0	8.9	10.7	10.3
(30)	1.5	3.2	6.6	9.9	12.5	12.5
(35)	1.7	3.3	6.9	10.5	13.2	13.7
(40)	1.8	3.7	7.3	10.7	14.1	15.3
(45)	1.9	3.7	7.4	11.2	14.5	18.6
(50)	1.9	3.7	7.6	11.2	15.2	19.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.944**	**0.949**	**0.965**	**0.930**	**0.915**	**0.917**

Figures in parentheses denotes time in minutes

Table- 6.33

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$ mol dm^{-3}, [Sodium Benzoate] =$8x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.8	1.9	3.4	3.6	3.8
(5)	1.0	1.0	2.8	4.7	4.9	4.7
(10)	1.2	1.2	3.6	5.5	5.8	6.7
(15)	1.4	1.4	4.4	6.9	7.5	8.8
(20)	1.5	1.9	5.6	7.5	8.9	9.8
(25)	1.6	2.4	6.5	8.9	10.8	11.2
(30)	1.8	3.0	6.9	10.2	12.8	13.2
(35)	1.9	3.5	7.2	11.0	13.5	15.1
(40)	1.9	3.8	7.6	11.3	14.3	17.9
(45)	1.9	3.8	7.7	11.5	15.7	19.7
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.12**	**1.10**	**1.18**	**1.13**	**1.14**	**1.11**

Figures in parentheses denotes time in minutes

Table - 6.34

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Sodium benzoate] = 7x10^{-5} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag(I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.6	0.9	0.8	0.8
(5)	0.9	0.8	1.2	1.1	1.0
(10)	1.2	1.0	1.5	1.3	1.3
(15)	1.4	1.2	1.6	1.5	1.4
(20)	1.5	1.4	1.6	1.7	1.8
(25)	1.7	1.6	1.8	1.8	1.8
(30)	1.7	1.7	1.9	1.9	1.9
(35)	1.7	1.9			
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.899**	**1.17**	**1.38**	**1.48**	**1.54**

Figures in parentheses denotes time in minutes

Table - 6.35

Variation of Ag (I) at S(IV)] = 1x10^{-3} mol dm^{-3}, [Sodium benzoate] = 8x10^{-6} mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag(I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.6	0.9	0.8	0.8
(5)	0.9	0.8	1.2	1.1	1.0
(10)	1.2	1.0	1.5	1.3	1.3
(15)	1.4	1.2	1.6	1.5	1.4
(20)	1.5	1.4	1.8	1.7	1.8
(25)	1.7	1.7	1.8	1.9	1.9
(30)	1.7	1.9			
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**1.01**	**1.38**	**1.47**	**1.69**	**1.80**

Figures in parentheses denotes time in minutes

Table - 6.36

Variation of sodium benzoate at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) =5 $x10^{-6}$ mol dm^{-3} pH = 4.95, t = 35^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Sodium Benzoate] mol dm^{-3}	**$3x10^{-7}$**	**$5x10^{-7}$**	**$8x10^{-7}$**	**$2x10^{-6}$**	**$6x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$8x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.5	0.8	0.5	0.5	0.5	0.5	0.5	0.5
(5)	1.7	1.6	1.5	1.5	1.5	1.5	0.8	0.8
(10)	2.3	1.9	1.8	1.8	1.8	1.8	1.0	0.9
(15)	2.6	2.4	2.2	2.2	2.2	2.2	1.3	1
(20)	3.1	2.9	3.0	2.8	2.8	2.8	1.6	1.2
(25)	3.5	3.2	3.2	3.3	3.2	3.2	1.8	1.3
(30)	3.8	3.7	3.4	3.3	3.3	3.4	2.3	1.5
(35)	3.8	3.8	3.5	3.4	3.5	3.5	2.5	2.0
(40)					3.6	3.6	2.7	2.2
(45)						3.6	2.8	2.5
(50)						3.8	2.8	2.6
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.18**	**1.10**	**1.01**	**0.988**	**0.958**	**0.917**	**0.569**	**0.515**

Figures in parentheses denotes time in minute

Table- 6.37

Variation of sodium benzoate at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5 $\times 10^{-6}$ mol dm^{-3} , pH = 4.95, t = 40^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH= 3×10^{-2} mol L^{-1}

[Sodium Benzoate] mol dm^{-3}	**3×10^{-7}**	**5×10^{-7}**	**8×10^{-7}**	**2×10^{-6}**	**6×10^{-6}**	**8×10^{-6}**	**5×10^{-5}**	**8×10^{-5}**
Time, (Min)	Volume of 5 $\times 10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.5	0.8	0.5	0.5	0.5	0.5	0.5	0.5
(5)	1.7	1.6	1.5	1.5	1.5	1.5	0.8	0.8
(10)	2.3	1.9	1.8	1.8	1.8	1.8	1.0	0.9
(15)	2.6	2.4	2.2	2.2	2.2	2.2	1.3	1.0
(20)	3.1	2.9	3.0	2.8	2.8	2.8	1.6	1.2
(25)	3.5	3.2	3.2	3.3	3.2	3.2	1.8	1.3
(30)	3.6	3.6	3.5	3.3	3.3	3.4	2.3	1.5
(35)					3.5	3.5	2.5	2
(40)						3.6	2.7	2.2
(45)						3.7	2.8	2.5
(50)						3.2	2.1	2.0
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.20**	**1.14**	**1.10**	**1.00**	**0.972**	**0.931**	**0.671**	**0.611**

Figures in parentheses denotes time in minutes

DISCUSSION

In aqueous solutions SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH the following equilibrium operates.

$$HSO_3^{-1} \rightleftharpoons H^+ + SO_3^{-2} \qquad (12)$$

The equilibrium constant is 5.07x 10^{-7} In the experimental range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. During the course of reaction fraction order obtain is 0.21 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz (2008)**[13]** Bigelow et al (1898)**[5]** studied the effect of alcohols on the reactions between sodium sulphite and O_2 and found that the alcohols inhibited the reaction rate. Alyea et al (1929)**[1]** studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Backstrom (1934)**[3]** proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2. Grgic et al (1998)**[10]** studied the inhibition effect of acetate, oxlate, format on Fe- catalysed autoxidation of S (IV) at pH 2.8, 3.7,4.5 and found that oxlate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe^{+3} due to formation of complexion with oxlate. Bostjan et al (2006)**[16]** studied the effect of carboxylic acid on Mn (II) catalysed oxidation of S(IV) and found that mono carboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag(I) catalysed reaction is decelerated by the addition of sodium benzoate in the present study. Gupta et al (2008)**[11]** reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3 - 10^4 In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S(IV) by sodium benzoate are found to be 3.68×10^4 mol dm^{-3} and 1.48×10^4 mol dm^{-3} respectively. These values are in the same range as reported by Gupta et al. This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick and Zhang (1996)**[6]**

$$HSO_3^{-1} \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{-2} \quad K_d = 5.01 \text{ x } 10^{-7\,,\,14} \qquad (13)$$

$$Ag^+ + {}^-O_2CCH_3 \overset{K_{oAc}}{\rightleftharpoons} AgO_2CCH_3 \quad K_{oAc} = 2.29^{17} \qquad (14)$$

$$Ag^+ + SO_3^{-2} \overset{K_1}{\rightleftharpoons} AgOSO_2^- \quad K_1 = 2.51\text{x } 10^{5},^{21} \qquad (15)$$

$$Ag^+ + HSO_3^{-1} \overset{K_2}{\rightleftharpoons} AgHSO_3 \qquad (16)$$

$$AgOSO_2^- + O_2 \overset{K_3}{\rightleftharpoons} AgOSO_2^{-1}.O_2 \qquad (17)$$

$$AgHSO_3 + O_2 \overset{K_4}{\rightleftharpoons} AgHSO_3.O_2 \qquad (18)$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (19)$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \qquad (20)$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \qquad (21)$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \qquad (22)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \qquad (23)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \qquad (24)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \qquad (25)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \qquad (26)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \qquad (27)$$

$$SO_4^{-\bullet} + \text{Sodium benzoate} \xrightarrow{k_{10}} \text{Non Chain product} \qquad (28)$$

By assuming long chain hypothesis and steady state approximation $d[SO_3^{-\bullet}]/dt$, $d[SO_4^{-\bullet}]/dt$, $d[SO_5^{-\bullet}]/dt$, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 29)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Sodium benzoate}]\}\,[SO_4^{-1}] \qquad (29)$$

Since the reaction is completely stopped in the presence of [Sodium benzoate] at $8\text{x}10^{-5}$ mol dm^{-3}, so the step (22) and (25) appear to be unimportant.

The step (24) is ignored because the reaction is completely seized in the presence of higher concentration of sodium benzoate by omission and substitution from the above mechanism the following rate law can be obtain (30)

$$R_{cat} = k_1 [Ag(I)] [S(IV)] / \{k_9[x] + k_{10} [Sodium\ benzoate]\} \qquad (30)$$

Prasad et al (2013)[20] and Gupta et al (2008)[11] proposed a similar mechanism for the Co_2O_3 and CoO catalysed autoxidation of SO_2 inhibited by formic acid and ethanol respectively, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 1.48×10^4 mol dm^{-3} which is in the range of 10^3 -10^4 and also coincide with the reported value of B of Co_2O_3 catalysed autoxidation of S(IV) by formic acid is 3.58×10^{3} mol dm^{-3} So on the basis of calculated value of B we concluded that sodium benzoate act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

CONCLUSIONS

The following conclusions are deduced from the results of the sodium benzoate inhibited Ag(I) catalysed autoxidation of S(IV) was that inhibit the oxidation with the fast influence. The value of Inhibition factor of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are in the range of 10^3 -10^4 which shows that free radical mechanism is operative.

REFERENCES

1. Alyea H. N. and Backstrom H. L. J., 1929, The inhibitive action of alcohols on the autoxidation of sodium sulfite, *Journal of American Chemical Society,* **51**, 90-107**.**
2. Andreozzi R., Marotta R., 2004, Removal of benzoic acid in aqueous solution by Fe(III) homogeneous photo catalysis. *Water Research*, **38**, 1225-1236.
3. Backstrom H. L. J., 1934, The chain mechanism of the autoxidation of sodium sulfite solutions. *J. Phys. Chem.*(B), **25**, 122-138.
4. Bates H.G.C., Uri N., 1953, Oxidation of aromatic compounds in aqueous solution by free radicals produced by photo excited electron transfer in iron complexes, *Journal of the Environmental Science and Technology,* **27**, 636-651.
5. Bigelow S. L., 1988, Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.
6. Connick R.E., Zhang Y. X., Lee S., Adamic R., Chieng P.,1995, Kinetics and mechanism of the oxidation of HSO_3 by O_2, the uncatalyzed reaction. *Inorganic Chemistry,* **34**, 4543–4553.
7. Cunningham K.M., Goldberg M.C., Weiner E.R., 1988, Mechanisms for aqueous photolysis of adsorbed benzoate, oxalate and succinate on iron oxyhydroxide (Goethite) surfaces, *Environmental Science and Technology* **22**, 1090–1097.
8. Galt J.A., Lehr W.J., Payton D.L., 1991, Fate and transport of the Exxon Valdez oil spill, *Environment Science and Technology,* **25**, 202–209.
9. Goldberg M.C., Cunningham K.M., Weiner E.R., 1993, Aquatic photolysis: photolytic redox reactions between goethite and adsorbed organic acids in aqueous solutions, *Journal of Photochemistry and Photobiology Chemistry*, **73**, 105–120.

10. Grgic I., Dovzan A., Bercic G., and Hudnik V., 1998, The effect of atmospheric organic compounds on the Fe-catalyzed S(IV) autoxidation in aqueous solution, *J. Atmos. Chem.* **29**, 315–337.
11. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., 2008, Kinetics of the uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 Catalyzed autoxidation of Sulfur(IV) in alkaline medium, *Transition Metal Chemistry*, **33**, 809-817.
12. Hansen H.P., 1975, Photochemical degradation of petroleum hydrocarbon surface films on seawater, *Marine Chemistry*, **3**, 183–195.
13. Irena Wilkosz, Maninka Anna, 2008, Mn (II) catalysed S(IV) oxidation and its inhibition by acetic acid in acidic aqueous solutions, *J Atmos Chem.* **60**, 1-17.
14. L.G. Sillen and A.E. Martell, 1964, stability constants of metal ion complex special publication no 17, The chemical soc. Burlington house London.
15. Payne J.R., Phillips C.R., 1985, Photochemistry of petroleum in water, *Environmental Science and Technology*, **19**, 569–579.
16. Podkrajsek B., Grgic I., and Tursic J., 2006, Influence of atmospheric carboxylic acid on catalytic oxidation of S(IV), *J of atmospheric chemistry*, **54**,103-120.
17. R. Van Eldik, and G,M. Harris, *Inorg Chem.* **19**, 880, 1980.
18. Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R., 1993, sources of fine organic aerosol, Non catalyst and catalyst-equipped automobile and heavy-duty diesel truck.
19. Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R., 1997a, Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil, *Environmental Science and Technology*.
20. Sameena Begam, Faiyaz Huusain, D.S.N. Prasad, 2013, Kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Pelagia research library*, **4 (1)**, 122-131.

21. V.F. Toropova I.A. Sirotina and V.B. Rotanova, 1955, Uchenye Zapiski Kazanskogo Uni. 115 no.3, 53.
22. Yiwei Deng, Kai Zhang, Hao Chen, Taixing Wu, Metthew Krzyaniak, et al, 2006, Iron-catalyzed photochemical transformation of benzoic acid in atmospheric liquids, Product identification and reaction mechanisms, *Atmospheric Environment*, **40**, 3665–3676.
23. Zhang K., Zuo Y., 2004, GC–MS determination of flavonoids and phenolic and benzoic acids in human plasma after consumption of cranberry juice, *Journal of Agricultural* Chem.
24. Zhang R., Suh I., Zhao J., Zhang D., Fortner E.C., Tie X., Molina L.T., Molina M.J., 2004, Atmospheric new particle formation enhanced by organic acids, *Science,* **304**, 1487–1490.

CHAPTER - VII

Kinetics of Aniline Inhibited uncatalysed and Ag (I) catalysed Autoxidation of S (IV) in Acidic Medium

ABSTRACT

The kinetics of atmospheric autoxidation of S(IV) by Ag (I) in the pH range 4.02-5.25 has been studied. Based on the observed results a free radical mechanism operative and following rate law has been proposed.

-d [S(IV)/dt = $(k_1+k_2[Ag])$ [S(IV)]/ 1 + B [Aniline]

INTRODUCTION

The acid rain problem is mainly attributed to anthropogenic sulphur dioxide and, to a lesser extent, nitrogen oxide emissions by Irena et al (2008)[19] The relative importance of different pathways for atmospheric oxidation of sulphur dioxide can vary under different conditions such as relative humidity, intensity of solar radiations, temperature and degree of air pollution. (Eigneur and Saxena1984).[36] Catalytic autoxidation of S(IV) is the subject of a number of studies e.g. (Penkett et al. 1979[30], Pasiuk-Bronikowska and Bronikowski 1981[29], Martin 1984[23], Martin and Hill 1987[23], Ibusuki and Takeuchi 1987[18], Kraft and Van Eldik 1989[20], Grgic et al. 1991[10], 1992[11], Berglund and Elding1995[3], Novic et al. 1996[25], Tursic et al. 2003[38]). It is claimed that at pH 4, transition metal catalysed pathways could account for up to half of the oxidation of S(IV) to S(VI) (Graedel et al. 1985).[8] According to present knowledge, iron(II/III) and manganese (II/III) are the most important catalysts in atmospheric droplets (Coichev and Van Eldik 1994[6], Brandt and Van Eldik 1995[5], Seinfeld and Pandis 1998[37]). These metals are the only efficient catalysts at low pH. In addition, both iron and manganese are common constituents of tropospheric aerosols and water droplets even in remote areas due to their generation from erosion of the earth's crust. Other transition metals such as Cu(II), Co(III), Sc(III), Ti(III), V(III) and Cr(III) are also catalysts, but with a substantially lower effect on the reaction rate (Ibusuki et al. 1990[12], Grgic et al. 1991[10], Sedlak and Hoigne1993[35]). The catalytic oxidation of S(IV) is a free radical chain reaction. Its mechanism and kinetics are so complex and sensitive to the conditions under which the process occurs that even a minor change in experimental conditions can cause a change of the dominant path of the reaction course, and thus lead to diverse results. Organic compounds may dissolve into water droplets and react with sulphoxy radicals and transition metal ions, and thus alter the rate of catalytic S(IV) oxidation (Martin et al. 1991[22], Pasiuk-Bronikowska et al. 1997[26], Grgic et al. 1998[9], Pasiuk-Bronikowska et al. 2003[12], Ziajka and Pasiuk-Bronikowska 2003[41], 2008[42]). Recently, the inhibiting effect of such organic ligands as oxalate, acetate and format in the iron-catalyzed autoxidation of S(IV) oxides in atmospheric water droplets has been suggested. Grgic et al. (1998[9], 1999[13]) and Wolf et al. (2000)[40] reported the strong inhibiting effect of oxalate on the Fe - catalysed S(IV) oxidation in aqueous acidic solution. Acetate and format also inhibit the reaction, but to a much lesser extent than oxalate (Grgic et al. 1998)[9]. Very recently, the influence of some low weight mono-(formic, acetic, glycolic, lactic) and di carboxylic acids (oxalic, malic, malonic) on the Mn(II)-catalysed S(IV) oxidation has also been investigated (Grgic et al. 2002[12], Podkrajsek et al. 2006).[32] The effect of aromatic amines i.e. aniline in atmospheric water on the transition metal-catalysed oxidation of S(IV) is not fully known yet and more work in this area is needed to understand these processes better. The purpose of the present study was to study the kinetics of the Ag(I) catalysed S(IV) oxidation and to determine the inhibiting effect of aniline on this process under different experimental conditions.

EXPERIMENTAL

The experimental procedure was exactly the same as described earlier.[34] All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature 30 ± 1^0 C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at 1600±10 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically. The reproducibility of replicate measurements was generally better than 10$\pm$1 %. All calculations were performed in MS Excel.

PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S (VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure.

The product analysis showed the recovery of sulphate to be 98$\pm$1% , in all cases in agreement with eq. (1)

$$S(IV) + 0.5\, O_2 \longrightarrow S(VI) \qquad (1)$$

RESULTS

Preliminary Investigation

The kinetics of both uncatalysed and Ag(I) catalysed and aniline inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30^{o} C. In both the cases the first order dependence of S(IV) was observed in the kinetics data treatment for the determination of first order rate constant k_1 was carried out from log [S(IV)] versus time, t. The plots were shown in fig. 7.1. From the fig.7.1 observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by aniline.

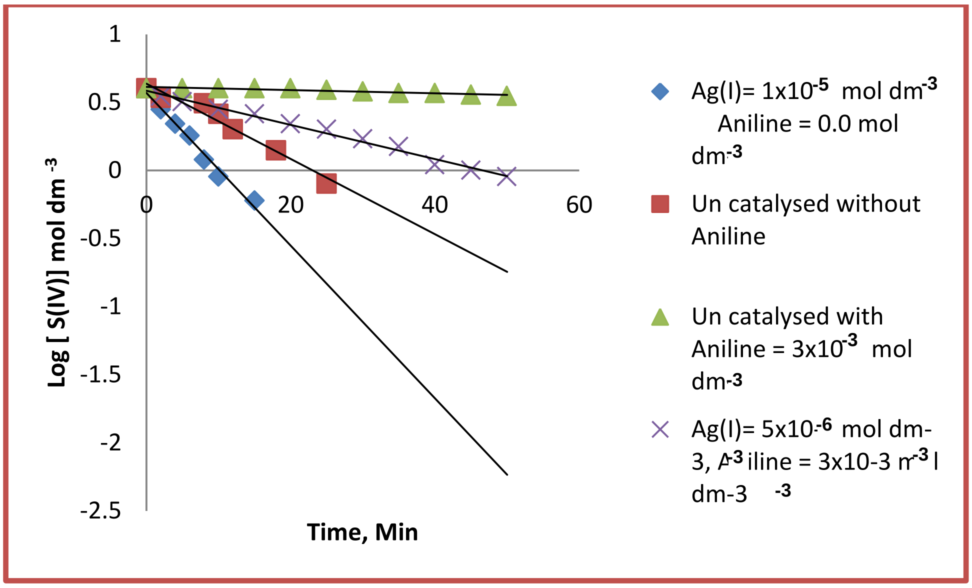


Fig. 7.1:The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2x 10^{-3} mol dm^{-3} at pH = 4.95, t = 30^{o} C.

(◇) Ag (I) = 1 x 10^{-5} mol dm^{-3}, [Aniline] = 0.0 mol dm^{-3}

(□) Uncatalysed without aniline

(△) Uncatalysed with [Aniline] = $3x10^{-3}$ mol dm^{-3}

(x) Ag (I) = 5 x 10^{-6} mol dm^{-3}, [Aniline] = 3 x 10^{-3} mol dm^{-3}

Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of Ag (I) and all the solutions were prepared in doubly distilled water.

Table- 7.1

Quantitative Analysis of Sulphate in Final Product Solution

10^3 [S(IV)] mol dm^{-3}	Ag (I) mol dm^{-3}	pH	10^3 [SO_4^{-2}] mol dm^{-3}	[SO_4^{-2}] / [S(IV)]	% of S(IV) recovery
5.0	0.00	4.95	4.90	0.980	98.0
5.0	$5x10^{-6}$	4.95	4.92	0.984	98.4
5.0	$1x10^{-5}$	4.95	4.95	0.990	99.0

Table- 7.2

Variation of [S (IV)] at pH = 4.95, t = 30^0 C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**3**	**4**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot			
(0)	0.0	0.0	0.0	0.0
(2)	0.5	0.6	1.3	1.6
(8)	0.8	0.9	2.1	2.2
(10)	1.0	1.4	3.2	3.2
(12)	1.2	2.0	3.8	4.3
(18)	1.4	2.6	4.6	5.4
(25)	1.6	3.2	4.8	6.5
∞	2.0	4.0	6.0	8.0
(10^3) k_1 s^{-1}	**1.04**	**1.06**	**1.09**	**1.09**

Figures in parentheses denotes time in minutes

Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range from $1x10^{-3}$ mol dm^{-3} to $4x10^{-3}$ mol dm^{-3} at pH = 4.95, t = 30^{o} C in acetate buffered medium. The kinetics was found to be first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of first order rate constant k_1 are given in table - 7.3. The dependence of reaction rate on [S(IV)] follows the rate law (2)

$$-d\,[S(IV)]\,/dt = k_1\,[S(IV)] \qquad (2)$$

Table- 7.3

The values of k_1 for uncatalysed reaction at different [S(IV)], pH = 4.95, t = 30^{o} C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH= 3x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	$(10^{3})\ k_1\ s^{-1}$
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

[Aniline] Dependence

The major aim of this study was to examine the effect of aniline on the autoxidation of S(IV) in acetate buffer medium and varying the [Aniline] from $5x10^{-7}$mol dm^{-3} to $8x10^{-3}$mol dm^{-3}, we observed the rate of the reaction decreased by increasing [Aniline] The results are given in table 7.4, However the nature of the [S(IV)] dependence in presence of aniline did not change and remains first order. The first order rate constant k_{inh} in the presence of aniline was defined by rate law (3)

$$-d\,[S(IV)]\,/dt \quad = \quad k_{inh}\,[S(IV)] \qquad (3)$$

The values of k_{inh} in the presence of aniline decreased with increasing [Aniline] are given in table 7.5 which are in agreement with the rate law (4)

$$k_{inh} = k_1 / (1+B\,[\text{Aniline}]) \qquad (4)$$

Where B is inhibition parameter for rate inhibition by aniline

The equation (4) on rearrangement becomes

$$1/\,k_{inh} = 1/\,k_1 + B\,[\text{Aniline}]\,/\,k_1 \qquad (5)$$

In accordance with the equation (5) the plot of $1/\,k_{inh}$ v/s [Aniline] was found to be linear with non- zero intercept fig. 7.2 The values of intercept ($1/\,k_1$) and slope ($B/\,k_1$) were found to be 1.53×10^3 s and 2.85×10^6 mol dm^{-3} s at pH = 4.95, t = 30^o C. From these values the value of inhibition parameter B was found to be 1.86×10^3 mol dm^{-3}

Table- 7.4

Variation of [Aniline] at [S (IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[Aniline] mol dm^{-3}	**$5x10^{-7}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$1x10^{-5}$**	**$5x10^{-5}$**	**$8x10^{-5}$**	**$1x10^{-4}$**	**$5x10^{-4}$**	**$8x10^{-4}$**	**$3x10^{-3}$**	**$5x10^{-3}$**	**$8x10^{-3}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot											
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.7	0.6	0.6	0.5	0.5	0.5	0.3	0.3	0.2	0.1	0.0	0.0
(10)	0.9	0.9	0.8	0.8	0.7	0.7	0.6	0.5	0.4	0.2	0.0	0.0
(15)	1.3	1.2	1.0	1.0	1.0	0.9	0.9	0.8	0.6	0.3	0.1	0.0
(20)	1.8	1.8	1.2	1.2	1.2	1.0	1.0	1.0	0.8	0.4	0.2	0.0
(25)	2.4	2.3	1.5	1.5	1.4	1.2	1.2	1.2	0.9	0.5	0.3	0.1
(30)	3.0	2.9	2.0	1.8	1.7	1.5	1.4	1.4	1.0	0.8	0.4	0.2
(35)	3.5	3.4	2.6	2.2	2.2	1.8	1.7	1.7	1.2	1.0	0.5	0.2
(40)	3.5	3.5	3.2	2.6	2.5	2.0	2.0	1.9	1.4	1.2	0.6	0.3
(45)	3.6	3.5	3.4	3.2	2.9	2.5	2.3	2.0	1.6	1.2	0.7	0.3
(50)	3.7	3.5	3.5	3.5	3.3	3.2	2.9	2.4	1.8	1.2	0.7	0.4
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1s^{-1}	**0.940**	**0.827**	**0.707**	**0.607**	**0.513**	**0.418**	**0.360**	**0.284**	**0.189**	**0.138**	**0.075**	**0.037**

Figures in parentheses denotes time in minute

Table- 7.5

The values of k_{inh} at different [Aniline], pH = 4.95, t = 30° C

CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[Aniline] mol dm^{-3}	10^3 k_{inh} s^{-1}	$1/k_{inh}$ s
$5.0x10^{-7}$	0.940	1064
$5.0x10^{-6}$	0.827	1209
$8.0x10^{-6}$	0.707	1414
$1.0x10^{-5}$	0.607	1647
$5.0x10^{-5}$	0.513	1949
$8.0x10^{-5}$	0.418	2392
$1.0x10^{-4}$	0.360	2778
$5.0x10^{-4}$	0.284	3521
$8.0x10^{-4}$	0.189	5291
$3.0x10^{-3}$	0.138	7246
$5.0x10^{-3}$	0.075	13333
$8.0x10^{-3}$	0.037	27027

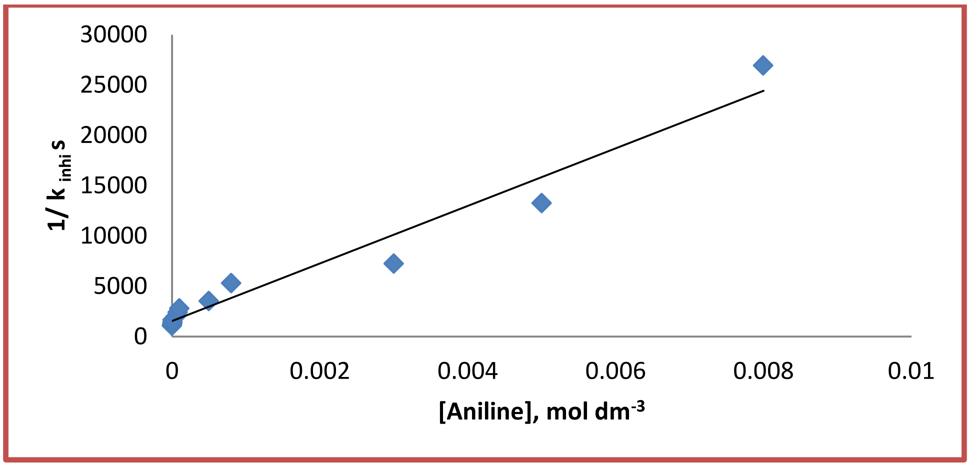


Fig.7.2:Effect of aniline at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30° C in acetate buffered medium.

Ag(I) Catalysed Reaction

At first the kinetics of Ag(I) Catalysed reaction in the absence of inhibitor was studied.

[S(IV)] Variation

The dependence of S (IV) on reaction rate was studied by varying [S(IV)] from $1\text{x}10^{-3}$ mol dm^{-3} to $10\text{x}10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5\text{x}10^{6}$ mol dm^{-3} and $1\text{x}10^{-5}$ mol dm^{-3} at pH = 4.95, t = 30^{o} C. The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in fig. 7.1.

Ag(I) Variations

The dependence of Ag(I) on the reaction rate was studied by varying Ag (I) from $5\text{x}10^{-6}$ mol dm^{-3} to $2.5\text{x}10^{-5}$ mol dm^{-3} at S(IV) = $2\text{x}10^{-3}$ mol dm^{-3} pH = 4.95, t = 30^{o} C in acetate buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig. 3.3. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law (6)

$$-d\,[S(IV)]\,/dt \;=\; k_{cat}\,[S(IV)] \;=\; (k_1+k_2[Ag(I)]\,[S(IV)] \qquad (6)$$

$$\text{Or}\;\; k_{cat} \;=\; k_1+k[Ag(I)] \qquad (7)$$

From the plot in fig. 7.3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be $0.72\text{x}\ 10^{1}$ s and $8.6\ \text{x}\ 10^{-3}$ mol dm^{-3} respectively at pH = 4.95, t = 30^{o} C in acetate buffered medium.

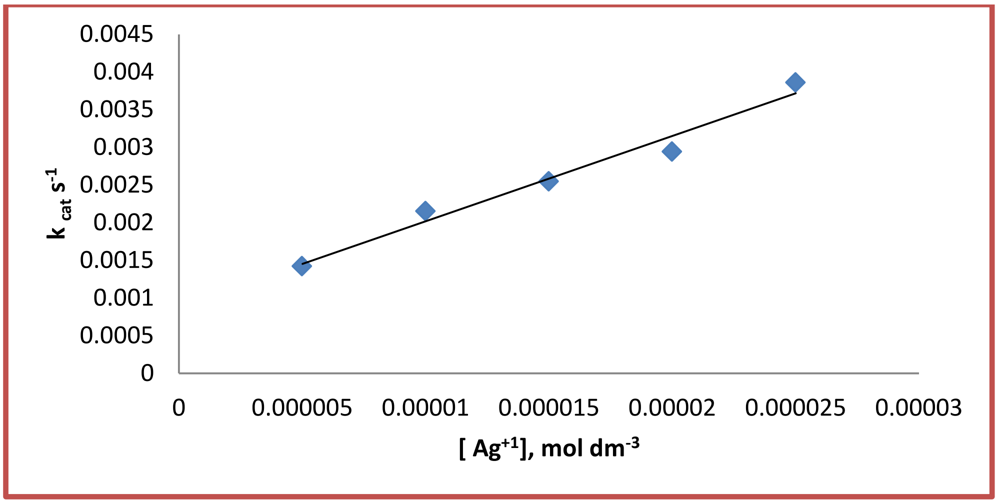


Fig 7.3 : The dependence of catalyst concentration at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium.

Table- 7.6

Variation of [S(IV)] = $2x10^{-3}$ mol dm^{-3} at Ag (I) =$5x10^{-6}$ mol dm^{-3} pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

10^3[S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.8	1.5	2.0	2.2
(4)	0.4	1.0	1.7	2.4	3.3	4.5
(6)	0.6	1.2	2.7	3.0	4.5	6.5
(8)	0.9	1.5	3.6	4.0	7.0	9.8
(10)	1.2	1.7	5.0	5.5	9.3	12.1
(15)	1.4	3.0	5.5	9.0	11.5	14.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.43**	**1.42**	**1.41**	**1.44**	**1.46**	**1.50**

Figures in parentheses denotes time in minutes

Table- 7.7

Variation of [S(IV)] = 2x10^{-3} mol dm^{-3} at Ag (I) =1x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3}mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.9	3.0	4.5	5.6
(4)	0.8	1.8	2.8	4.8	6.3	7.8
(6)	1.2	2.2	3.6	5.9	7.8	9.5
(8)	1.4	2.8	4.5	7.8	8.9	10.2
(10)	1.5	3.1	5.0	8.9	12.5	12.8
(15)	1.7	3.4	7.0	10.3	13.6	17.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**2.19**	**2.15**	**2.15**	**2.18**	**2.14**	**2.10**

Figures in parentheses denotes time in minutes

Table- 7.8

Variation of Ag (I) at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5x10^{-6}$**	**$1x10^{-5}$**	**$1.5x10^{-5}$**	**$2x10^{-5}$**	**$2.5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.4	2.5	2.4
(4)	1.0	1.8	1.8	2.7	2.5
(6)	1.2	2.2	2.0	2.9	3.0
(8)	1.5	2.8	2.2	3.7	3.5
(10)	1.7	3.1	3.4		
(15)	3.0	3.4			
∞	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.42**	**2.15**	**2.54**	**2.94**	**3.88**

Figures in parentheses denotes time in minutes

Table - 7.9

The values of k_{cat} at different concentration of Ag (I) mol dm^{-3}, pH = 4.95, t = 30^o C, $CH_3COONa = 7x10^{-2}$ mol L^{-1} $CH_3COOH= 3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	10^3 k_{cat} s^{-1}
0.000005	1.42
0.00001	2.15
0.00015	2.54
0.00020	2.94
0.00025	3.88

Variation of pH

Variation of pH was carried out from 4.02-5.25 at different [S(IV), Ag (I), [Aniline] and temperatures. The rate decreases slightly by varying pH is inverse H^+ ion dependence was observed. From the plot of log k_1 v/s log (H^+), the order with respect to H^+ is 0.16 which is a fractional order and can be neglected as shown in fig 7.4.

Table - 7.10

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Aniline] = $5.0x10^{-4}$ mol dm^{-3}, t= 30^o C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}

pH	$10^{\ 3}$ k s^{-1}
4.02	0.470
4.35	0.514
4.56	0.564
4.75	0.607
4.95	0.686
5.25	0.717

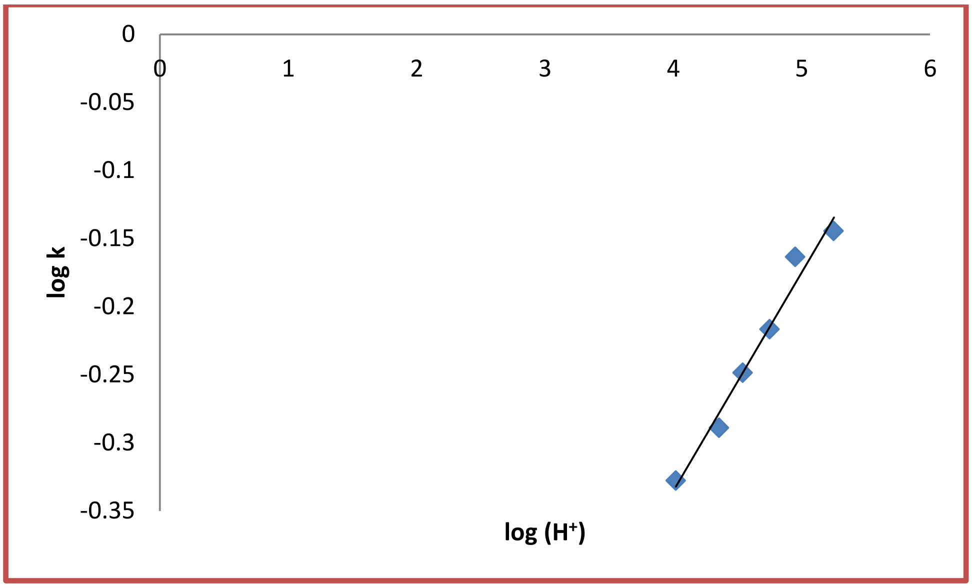


Fig.7.4: Effect of pH at [S(IV)] = 2×10^{-3} mol dm^{-3} Ag (I) = 5×10^{-6} mol dm^{-3}, [Aniline] = 5.0×10^{-4} mol dm^{-3}, t= 30^{o} C in acetate buffered medium.

Table - 7.11

Rate of Ag (I) Catalysed Autoxidation in the Presence of Aniline.

[Aniline], mol dm^{-3}	**Ag (I) =5×10^{-6} mol dm^{-3}**	**Ag (I) =1×10^{-5} mol dm^{-3}**	**Ag (I) =1.5×10^{-5} mol dm^{-3}**
pH = 4.02			
5.0×10^{-4}	0.470×10^{-3}	0.564×10^{-3}	0.717×10^{-3}
8.0×10^{-4}	0.400×10^{-3}	_	_
3.0×10^{-3}	0.319×10^{-3}	_	_
pH = 4.50			
5.0×10^{-4}	0.499×10^{-3}	0.590×10^{-3}	0.788×10^{-3}
8.0×10^{-4}	0.471×10^{-3}	_	_
3.0×10^{-3}	0.402×10^{-3}	_	_
pH = 5.25			
5.0×10^{-4}	0.586×10^{-3}	0.718×10^{-3}	0.942×10^{-3}
8.0×10^{-4}	0.577×10^{-3}	_	_
3.0×10^{-3}	0.516×10^{-3}	_	_

Table - 7.12

Ratio of rates for Ag (I) Catalysed oxidation in the Absence and in the Presence of Aniline.

[Aniline] =5.0x10^{-4} mol dm^{-3}	Ag (I) =5x10^{-6} mol dm^{-3}	Ag (I) =1 x 10^{-5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.50			
	3.02	**3.81**	**3.54**

Table - 7.13

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.5	0.5	0.5	0.6
(5)	0.7	0.8	0.8	0.8	0.8	0.9
(10)	0.9	1.0	1.2	1.2	1.2	1.3
(15)	1.2	1.2	1.4	1.4	1.5	1.7
(20)	1.4	1.5	1.7	1.7	2.0	2.3
(25)	1.6	1.9	2.3	2.3	2.2	2.5
(30)	1.8	2.2	2.5	2.5	2.5	2.8
(35)	2.0	2.4	2.6	2.7	2.9	3.0
(40)	2.5	2.6	2.7	3.0	3.3	3.1
(45)	2.9	2.9	3.0	3.3	3.4	3.5
(50)	3.3	3.4	3.5	3.4	3.5	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.470**	**0.514**	**0.564**	**0.607**	**0.686**	**0.717**

Figures in parentheses denotes time in minutes

Table - 7.14

Variation of pH at [S(IV)] = $4x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Aniline] = $5x10^{-4}$ mol dm^{-3}, t= 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.9	1.2	1.2	1.3	1.4	1.5
(5)	1.6	1.8	1.8	1.9	2.0	2.2
(10)	2.0	2.4	2.4	2.5	2.6	2.7
(15)	2.4	2.9	2.9	3.0	3.2	3.3
(20)	2.8	3.2	3.2	3.5	3.9	4.0
(25)	3.4	3.7	3.9	3.9	4.2	4.4
(30)	4.2	4.2	4.4	4.6	4.6	4.8
(35)	4.8	4.8	4.9	5.0	5.2	5.5
(40)	5.3	5.4	5.5	5.7	5.9	6.0
(45)	5.7	5.9	6.3	6.6	7.0	7.2
(50)	6.3	6.9	7.0	7.1	7.3	7.3
∞	8.0	8.0	8.0	8.0	8.0	8.0
(10^3) k_1, s^{-1}	**0.463**	**0.520**	**0.565**	**0.607**	**0.685**	**0.717**

Figures in parentheses denotes time in minutes

Table - 7.15

Variation of pH at [S(IV)] = 6x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.5	1.7	1.9	1.9	1.9	1.9
(5)	2.6	2.7	2.8	2.8	2.8	2.9
(10)	3.0	3.2	3.4	3.4	3.6	3.7
(15)	3.6	3.9	4.2	4.2	4.4	4.6
(20)	4.4	4.6	5.0	5.3	5.5	5.6
(25)	4.9	5.2	6.2	6.6	6.8	6.8
(30)	5.6	5.9	6.8	7.3	7.5	7.7
(35)	6.9	6.9	7.6	8.2	8.8	9.2
(40)	7.7	7.8	8.4	9.2	9.4	9.9
(45)	8.9	9.7	9.7	10	10.2	10.4
(50)	9.5	10.0	10.3	10.2	10.7	10.7
∞	12.0	12.0	12.0	12.0	12.0	12.0
(10^3) k_1, s^{-1}	**0.461**	**0.523**	**0.568**	**0.611**	**0.683**	**0.722**

Figures in parentheses denotes time in minutes

Table - 7.16

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $1x10^{-5}$ mol dm^{-3}, [Aniline] = $5x10^{-4}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.6	0.6	0.6	0.7	0.8
(5)	0.9	0.9	0.9	0.9	0.9	1.0
(10)	1.2	1.2	1.3	1.3	1.3	1.4
(15)	1.4	1.4	1.5	1.5	1.6	1.7
(20)	1.6	1.6	1.9	1.9	2.2	2.3
(25)	1.8	2.0	2.4	2.4	2.4	2.7
(30)	2.0	2.3	2.7	2.7	2.8	2.8
(35)	2.2	2.7	2.9	3.0	3.0	3.1
(40)	2.6	2.9	3.0	3.2	3.3	3.2
(45)	3.0	3.2	3.3	3.4	3.4	3.6
(50)	3.4	3.2	3.3	3.4	3.6	3.7
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.499**	**0.532**	**0.590**	**0.654**	**0.717**	**0.788**

Figures in parentheses denotes time in minutes

Table - 7.17

Variation of pH at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = $1.5\text{x}10^{-5}$ mol dm^{3}, [Aniline] = $5\text{x}10^{-4}$ mol dm^{-3}, t= 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.7	0.7	0.8	0.8	0.8
(5)	1.1	1.0	1.0	1.0	1.1	1.2
(10)	1.4	1.3	1.4	1.4	1.4	1.6
(15)	1.7	1.5	1.7	1.7	1.6	1.9
(20)	1.9	1.9	2.1	2.0	2.3	2.4
(25)	2.2	2.2	2.6	2.5	2.6	2.9
(30)	2.5	2.6	2.9	2.9	3.0	3.2
(35)	2.7	2.9	3.2	3.3	3.2	3.4
(40)	3.0	3.2	3.3	3.5	3.3	3.5
(45)	3.2	3.4	3.5	3.5	3.7	3.7
(50)	3.5	3.5	3.5	3.6	3.7	3.8
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.586**	**0.663**	**0.718**	**0.784**	**0.844**	**0.942**

Figures in parentheses denotes time in minutes

Table - 7.18

Variation of pH at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = $5\text{x}10^{-6}$ mol dm^{3}, [Aniline] = $8\text{x}10^{-4}$ mol dm^{-3}, t = 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.4	0.6	0.5	0.5	0.6
(5)	0.9	0.7	0.8	0.7	0.8	0.8
(10)	1.1	0.9	1.0	1.0	1.0	1.0
(15)	1.3	1.0	1.2	1.2	1.2	1.3
(20)	1.6	1.3	1.5	1.3	1.6	1.5
(25)	1.8	1.5	1.9	1.5	1.9	2.0
(30)	2.0	1.7	2.2	1.7	2.2	2.2
(35)	2.2	2.0	2.4	2.0	2.4	2.4
(40)	2.4	2.2	2.6	2.3	2.6	2.6
(45)	2.8	2.8	2.9	3.3	3.0	3.0
(50)	3.0	3.2	3.2	3.4	3.5	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.400**	**0.431**	**0.471**	**0.528**	**0.549**	**0.577**

Figures in parentheses denotes time in minutes

Table - 7.19

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Aniline] = $3x10^{-3}$ mol dm^{-3}, t= 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.4	0.6	0.5	0.5	0.6
(5)	0.9	0.7	0.8	0.7	0.8	0.8
(10)	1.1	0.9	0.9	0.9	0.9	0.9
(15)	1.3	1.0	1.1	1.0	1.3	1.2
(20)	1.4	1.3	1.4	1.2	1.4	1.4
(25)	1.6	1.4	1.8	1.4	1.7	1.8
(30)	1.8	1.6	2.0	1.6	2.0	2.0
(35)	2.0	1.9	2.2	1.8	2.3	2.2
(40)	2.2	20	2.4	2.0	2.5	2.4
(45)	2.4	2.5	2.7	2.4	2.9	2.9
(50)	2.8	2.9	3.0	3.5	3.3	3.5
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.319**	**0.347**	**0.402**	**0.444**	**0.480**	**0.516**

Figures in parentheses denotes time in minutes

Table - 7.20

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Aniline] = $5x10^{-4}$ mol dm^{-3}, t= 35^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.6	0.6	0.6	0.6	0.7
(5)	0.9	0.9	0.9	0.9	0.9	1.0
(10)	1.1	1.2	1.3	1.3	1.3	1.4
(15)	1.3	1.4	1.5	1.5	1.7	1.9
(20)	1.5	1.6	1.8	1.9	2.2	2.4
(25)	1.7	2.0	2.4	2.4	2.5	2.7
(30)	1.9	2.3	2.6	2.6	2.8	3.0
(35)	2.2	2.6	2.9	2.9	3.0	3.2
(40)	2.6	2.9	3.0	3.0	3.1	3.3
(45)	3.0	3.2	3.2	3.3	3.4	3.5
(50)	3.4	3.2	3.4	3.5	3.6	3.6
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.501**	**0.527**	**0.594**	**0.634**	**0.697**	**0.747**

Figures in parentheses denotes time in minutes

Table - 7.21

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Aniline] = $5x10^{-4}$ mol dm^{-3}, t= 40^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.8	0.7	0.7	0.8	0.8
(5)	1.1	1.0	1.0	1.0	1.0	1.1
(10)	1.3	1.3	1.4	1.4	1.4	1.5
(15)	1.5	1.5	1.6	1.6	1.6	1.9
(20)	1.8	1.9	1.9	2.0	2.2	2.4
(25)	2.0	2.2	2.6	2.4	2.5	2.7
(30)	2.2	2.5	2.9	2.6	2.8	3.1
(35)	2.3	2.7	3.0	2.9	3.2	3.2
(40)	2.6	3.0	3.2	3.2	3.3	3.3
(45)	3.2	3.2	3.3	3.4	3.4	3.5
(50)	3.4	3.3	3.4	3.5	3.6	3.7
∞	4.0	4.0	4.0	4.0	4.0	4.0
$(10^{3})k_1$, s^{-1}	**0.5140**	**0.548**	**0.633**	**0.659**	**0.722**	**0.781**

Figures in parentheses denotes time in minutes

Table- 7.22

Variation of [S(IV)] at Ag (I) = 5 x10^{-6} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.5	1.4	1.9	2.4	2.9
(5)	0.5	0.8	2.0	2.8	4.2	4.2
(10)	0.6	1.2	2.6	3.6	6.2	5.6
(15)	0.7	1.5	3.2	4.4	7.5	7.2
(20)	0.9	2.0	3.9	5.5	8.2	8.8
(25)	1.0	2.2	4.2	6.8	9.3	10.9
(30)	1.2	2.5	4.6	7.5	10.3	12.4
(35)	1.4	2.9	5.2	8.8	11.4	13.5
(40)	1.5	3.3	5.9	9.4	12.5	15.7
(45)	1.7	3.4	7.0	10.2	13.4	17.0
(50)	1.8	3.5	7.3	10.7	14.6	17.9
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.678**	**0.686**	**0.685**	**0.683**	**0.680**	**0.683**

Figures in parentheses denotes time in minutes

Table- 7.23

Variation of [S(IV)] at Ag (I) =1x10^{-5} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.7	1.6	2.5	2.7	2.9
(5)	0.6	0.9	2.2	2.9	4.9	4.8
(10)	0.8	1.3	2.9	3.7	6.9	6.2
(15)	1.0	1.6	3.3	4.9	7.9	7.7
(20)	1.2	2.2	4.0	5.8	8.8	9.2
(25)	1.3	2.4	4.5	7.2	9.7	11.2
(30)	1.4	2.8	4.9	8.2	10.5	13.4
(35)	1.6	3.0	5.5	9.0	11.5	14.5
(40)	1.7	3.3	6.0	9.5	13.2	16.2
(45)	1.7	3.4	7.2	10.4	14.3	17.5
(50)	1.8	3.6	7.3	10.8	14.4	17.8
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**0.715**	**0.717**	**0.714**	**0.710**	**0.716**	**0.715**

Figures in parentheses denotes time in minutes

Table- 7.24

Variation of [S(IV)] at Ag (I) =2 x10^{-5} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	1.8	2.6	2.9	2.9
(5)	0.9	1.1	2.3	3.2	4.9	4.8
(10)	1.2	1.4	3.2	3.7	6.9	6.2
(15)	1.3	1.6	4.4	5.2	7.9	7.7
(20)	1.4	2.3	5.2	6.2	8.8	9.2
(25)	1.5	2.6	6.2	7.7	9.7	11.2
(30)	1.5	3.0	6.7	8.5	10.7	13.4
(35)	1.8	3.2	7.0	9.2	11.9	15.6
(40)	1.8	3.3	7.0	9.9	14.2	17.3
(45)	1.8	3.7	7.2	10.7	14.7	18.3
(50)	1.9	3.7	7.3	11.4	14.9	18.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.853**	**0.844**	**0.842**	**0.846**	**0.842**	**0.846**

Figures in parentheses denotes time in minutes

Table- 7.25

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2}mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.7	0.7	0.7
(5)	0.5	0.6	0.9	0.9	0.9
(10)	0.6	0.8	1.2	1.2	1.2
(15)	0.7	1.0	1.3	1.3	1.3
(20)	0.9	1.2	1.4	1.4	1.4
(25)	1.0	1.3	1.5	1.6	1.6
(30)	1.2	1.4	1.5	1.6	1.8
(35)	1.4	1.6	1.8	1.8	1.9
(40)	1.5	1.7	1.8	1.9	
(45)	1.7	1.7	1.8		
(50)	1.8	1.8	1.9		
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.678**	**0.715**	**0.853**	**1.02**	**1.21**

Figures in parentheses denotes time in minutes

Table- 7.26

Variation of Ag (I) at S(IV)] = 2 x10^{-3} mol dm^{-3}, [Aniline] = 7.5x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.7	0.8	0.8	1.2
(5)	0.8	0.9	1.1	1.1	1.5
(10)	1.2	1.3	1.4	1.4	1.9
(15)	1.5	1.6	1.6	1.6	1.6
(20)	2.0	2.2	2.3	2.3	2.3
(25)	2.2	2.4	2.6	2.6	2.6
(30)	2.5	2.8	3.0	3.4	3.2
(35)	2.9	3.0	3.2	3.5	3.7
(40)	3.3	3.3	3.3	3.7	3.9
(45)	3.4	3.4	3.7		
(50)	3.5	3.6	3.7		
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.686**	**0.717**	**0.844**	**1.01**	**1.23**

Figures in parentheses denotes time in minutes

Table- 7.27

Variation of Ag (I) at S(IV)] = 4 x10^{-3} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	1.4	1.6	1.8	1.8	1.8
(5)	2.0	2.2	2.3	2.3	2.3
(10)	2.6	2.9	3.2	3.2	3.2
(15)	3.2	3.3	4.4	4.4	4.4
(20)	3.9	4.0	5.2	5.2	5.2
(25)	4.2	4.5	6.2	6.2	6.2
(30)	4.6	4.9	6.7	6.7	7.0
(35)	5.2	5.5	7.0	7.2	7.3
(40)	5.9	6.0	7.0	7.4	7.7
(45)	7.0	7.2	7.2		
(50)	7.3	7.3	7.3		
∞	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1 s^{-1}	**0.685**	**0.714**	**0.842**	**1.05**	**1.24**

Figures in parentheses denotes time in minutes

Table- 7.28

Variation of aniline at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5 $\times10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^{0} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH= 3×10^{-2} mol L^{-1}

[Aniline] mol dm^{-3}	**5×10^{-7}**	**8×10^{-6}**	**5×10^{-5}**	**1×10^{-4}**	**5×10^{-4}**	**8×10^{-4}**	**3×10^{-3}**
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.9	0.8	0.7	0.5	0.5	0.5	0.5
(5)	1.4	1.0	0.9	0.8	0.8	0.8	0.8
(10)	1.9	1.3	1.3	1.2	1.2	1.2	1.2
(15)	2.3	1.6	1.7	1.5	1.5	1.4	1.4
(20)	2.6	2.2	2.2	2.0	2.0	1.8	1.8
(25)	3.0	2.5	2.5	2.4	2.2	2.0	2.0
(30)	3.3	2.9	2.9	2.8	2.5	2.3	2.3
(35)	3.5	3.0	3.2	3.2	2.9	2.5	2.5
(40)	3.7	3.5	3.4	3.4	3.3	2.9	2.9
(45)	3.9	3.8	3.6	3.5	3.4	3.0	3.0
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.14**	**0.909**	**0.832**	**0.749**	**0.686**	**0.521**	**0.486**

Figures in parentheses denotes time in minutes

Table- 7.29

Variation of aniline at [S(IV)]= $2x10^{-3}$ mol dm^{-3}, Ag (I) =$1x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^0 C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Aniline] mol dm^{-3}	**$5x10^{-7}$**	**$8x10^{-6}$**	**$5x10^{-5}$**	**$1x10^{-4}$**	**$5x10^{-4}$**	**$8x10^{-4}$**	**$3x10^{-3}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.2	1.2	0.9	0.8	0.8	0.8	0.7
(5)	1.4	1.5	1.3	1.2	1.2	1.2	0.9
(10)	1.9	1.8	1.6	1.5	1.5	1.6	1.3
(15)	2.4	2.1	1.9	1.9	1.9	1.9	1.6
(20)	2.7	2.5	2.4	2.4	2.4	2.2	1.8
(25)	3.2	2.9	2.8	2.9	2.9	2.5	2
(30)	3.4	3.2	3.2	3.2	3.2	2.9	2.3
(35)	3.7	3.5	3.4	3.4	3.4	3.2	2.5
(40)	3.9	3.9	3.6	3.6	3.6	3.2	3.1
(45)			3.7	3.7	3.6	3.2	3.2
(50)			3.8		3.6	3.4	3.3
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.29**	**1.16**	**0.954**	**0.932**	**0.799**	**0.608**	**0.549**

Figures in parentheses denotes time in minutes

[Aniline] Dependence

To know the effect of aniline on Ag (I) catalysed autoxidation of S(IV) aniline variation was carried out from 5 x 10^{-7} mol dm^{-3} to 3 x 10^{-3} mol dm^{-3} at two different Ag (I) that is 5 x 10^{-6} mol dm^{-3} and 1 x 10^{-5} mol dm^{-3} but fixed S(IV) = $2x10^{-3}$ mol dm^{-3} at pH = 4.95 and t = 30^o C. The results indicated that by increasing aniline the rate becomes decelerates.

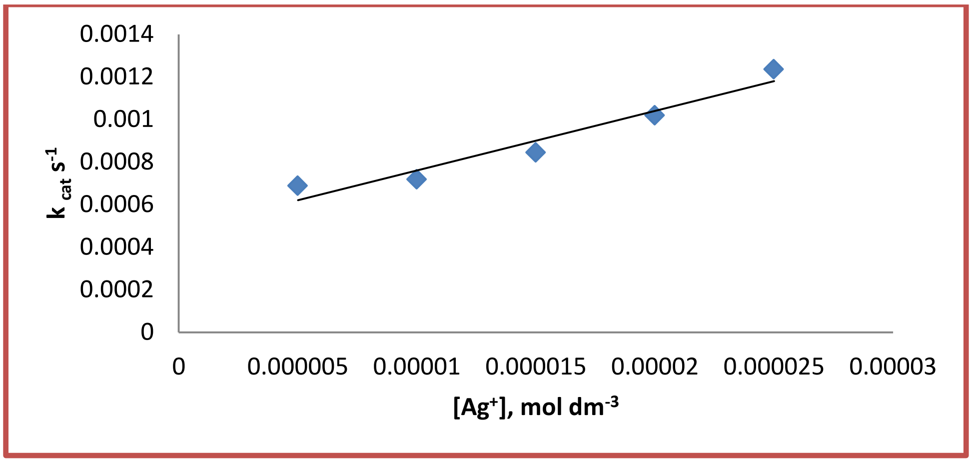


Fig.7.5 : Effect of catalyst at [S(IV)] = $2x10^{-3}$ mol dm^{-3} [Aniline] = $5.0x10^{-4}$ mol dm^{-3}, t= 30^o C in acetate buffered medium. The value of intercept and slope are 4.8 x 10^{-4} s and 2.7 x 10^1 mol dm^{-3} s respectively. Depending on the observed results the reaction follows the following rate law (8)

$$-d\,[S(IV)]\,/dt = (k_1+k_2[Ag(I)]\,[S(IV)]\,/\,1 + B\,[Aniline] \qquad (8)$$

$$\text{Where } k_{inh}= (k_1+k_2[Ag(I)]\,/\,1 + B\,[Aniline] = k_{cat}/\,1 + B\,[Aniline] \qquad (9)$$

$$1/\ k_{inh} = 1 + B\,[Aniline]\,/\,k_{cat} \qquad (10)$$

$$1/\ k_{inh} = 1/\,k_{cat} + B\,[Aniline]\,/\ k_{cat} \qquad (11)$$

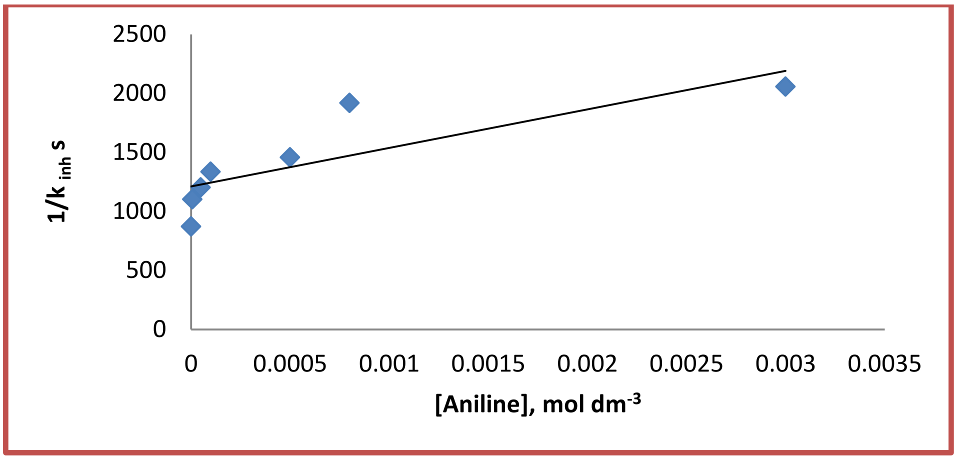


Fig.7.6 : Effect of aniline at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium. The plot of 1/ k_{inh} v/s [Aniline] is linear with intercept 1.21 x 10^{3} s and slope 3.25 x 10^{5} mol dm^{-3} s from which the value of B = 0.26 x10^{3} mol dm^{-3}.

Table- 7.30

The values of k_{inh} at different [Aniline], [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

[Aniline] mol dm^{-3}	10^{3} k_{inh} s^{-1}	1/k_{inh} s
5.0x10^{-7}	1.14	877
8.0x10^{-6}	0.909	1100
5.0x10^{-5}	0.832	1202
1.0x10^{-4}	0.749	1335
5.0x10^{-4}	0.686	1458
8.0x10^{-4}	0.521	1919
3.0x10^{-3}	0.486	2058

Effect of Temperature

The values of k_{obs} were determined at three different temperatures in the range of 30^o C to 40^o C The results are given in table 7.31, by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 26.43 KJ mol^{-1}

Table - 7.31

Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3}, [Aniline] = 5.0 x 10^{-4} mol dm^{-3}, pH = 4.95

t^o C	10^3 k_{obs} s^{-1}
30	0.686
35	0.781
40	0.915

Table- 7.32

Variation of [S(IV)] at Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Aniline] = $5x10^{-4}$ mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10 $^{-3}$mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.8	1.6	1.9	2.4	2.9
(5)	0.8	1.0	2.2	2.8	4.4	4.5
(10)	1.0	1.3	2.9	3.7	6.6	5.9
(15)	1.2	1.6	3.3	4.5	7.8	7.7
(20)	1.4	1.9	4.2	5.6	8.5	9.3
(25)	1.5	2.3	4.6	7.0	9.4	11.5
(30)	1.6	2.6	5.2	7.9	10.4	13.5
(35)	1.7	3.0	6.2	8.8	11.7	14.2
(40)	1.8	3.4	7.0	9.4	12.8	15.9
(45)	1.8	3.5	7.1	10.4	13.5	17.5
(50)	1.8	3.7	7.3	11.3	15.3	18.7
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**0.784**	**0.781**	**0.784**	**0.785**	**0.787**	**0.782**

Figures in parentheses denotes time in minutes

Table- 7.33

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$ mol dm^{-3}, [Aniline] = $5x10^{-4}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.8	1.8	1.9	2.6	2.9
(5)	0.8	1.2	2.5	2.9	4.6	4.8
(10)	1.2	1.5	3.0	3.8	6.9	5.9
(15)	1.4	1.8	3.4	4.6	7.9	7.9
(20)	1.6	2.0	4.5	5.7	8.8	9.5
(25)	1.7	2.5	5.1	7.2	9.9	11.5
(30)	1.8	2.9	6.2	7.9	10.8	14.5
(35)	1.8	3.2	6.6	8.8	11.8	15.2
(40)	1.8	3.5	7.2	9.4	13.5	16.2
(45)	1.8	3.8	7.2	11.0	14.4	17.9
(50)			7.6	11.6	15.5	19.3
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.904**	**0.915**	**0.916**	**0.913**	**0.904**	**0.909**

Figures in parentheses denotes time in minutes

Table- 7.34

Variation of Ag (I) at S(IV)] = 2 x10^{-3} mol dm^{-3}, [Aniline] = 5x10^{-4} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.5	0.8	0.9	0.9
(5)	0.6	0.8	1.0	1.2	1.2
(10)	0.9	0.9	1.3	1.4	1.3
(15)	1.2	1.2	1.5	1.6	1.5
(20)	1.3	1.3	1.6	1.8	1.6
(25)	1.4	1.5	1.6	1.8	1.8
(30)	1.5	1.6	1.8	1.8	1.9
(35)	1.6	1.7	1.8	1.9	1.9
(40)	1.6	1.8	1.8	1.9	
(45)	1.8	1.8	1.9		
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.727**	**0.842**	**0.947**	**1.17**	**1.35**

Figures in parentheses denotes time in minutes

Table- 7.35

Variation of Ag (I) at S(IV)] = 2 x 10^{-3} mol dm^{-3}, [Aniline] =$7.5x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 40^{0} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5x10^{-6}$**	**$1x10^{-5}$**	**$1.5x10^{-5}$**	**$2x10^{-5}$**	**$2.5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.8	0.8	1.2	0.9
(5)	0.6	1.0	1.2	1.4	1.2
(10)	0.9	1.2	1.5	1.5	1.3
(15)	1.2	1.4	1.6	1.6	1.5
(20)	1.4	1.6	1.7	1.8	1.7
(25)	1.6	1.8	1.7	1.8	1.8
(30)	1.7	1.8	1.8	1.9	1.9
(35)	1.7	1.8	1.9	1.9	
(40)	1.8	1.8	1.9		
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.943**	**0.984**	**1.13**	**1.27**	**1.45**

Figures in parentheses denotes time in minute

Table- 7.36

Variation of aniline at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 5 $\times10^{-6}$ mol dm^{-3},
pH = 4.95, t = 35^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1},
CH_3COOH = 3×10^{-2} mol L^{-1}

[Aniline] mol dm^{-3}	**5x10^{-7}**	**8x10^{-6}**	**5x10^{-5}**	**1x10^{-4}**	**5x10^{-4}**	**8x10^{-4}**	**3x10^{-3}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.3	1.2	0.9	0.8	0.7	0.8	0.8
(5)	1.4	1.5	1.2	1.2	1.0	1.2	1.2
(10)	2.0	1.9	1.5	1.5	1.3	1.5	1.5
(15)	2.4	2.5	1.9	1.9	1.7	1.9	1.9
(20)	2.6	2.7	2.4	2.2	2.0	2.3	2.4
(25)	3.2	3.2	2.9	2.6	2.5	2.6	2.6
(30)	3.5	3.5	3.2	3.0	2.8	3.0	3.0
(35)	3.8	3.5	3.4	3.3	3.2	3.2	3.0
(40)	3.8	3.8	3.6	3.5	3.4	3.2	3.0
(45)			3.7	3.6	3.6	3.3	3.2
(50)						3.3	3.2
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.23**	**1.09**	**0.928**	**0.818**	**0.757**	**0.607**	**0.540**

Figures in parentheses denotes time in minutes

Table- 7.37

Variation of aniline at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) =5 $\times10^{-6}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH = 3×10^{-2} mol L^{-1}

[Aniline] mol dm^{-3}	5×10^{-7}	8×10^{-6}	5×10^{-5}	1×10^{-4}	5×10^{-4}	8×10^{-4}	3×10^{-3}
Time, (Min)	Volume of 5 $\times10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot						
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.4	1.4	1.2	0.8	0.9	0.8	0.8
(5)	1.6	1.6	1.4	1.2	1.3	1.2	1.2
(10)	2.2	2.0	1.6	1.5	1.6	1.5	1.5
(15)	2.6	2.6	2.0	2.1	1.9	1.9	1.9
(20)	3.0	2.9	2.5	2.4	2.2	2.3	2.4
(25)	3.3	3.3	2.9	2.9	2.6	2.6	2.6
(30)	3.6	3.6	3.3	3.2	3.0	3.3	3.0
(35)	3.9	3.8	3.5	3.5	3.3	3.4	3.1
(40)			3.7	3.6	3.6	3.5	3.2
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.43**	**1.26**	**0.973**	**0.930**	**0.885**	**0.819**	**0.638**

Figures in parentheses denotes time in minutes

DISCUSSION

In aqueous solutions SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH the following equilibrium operates.

$$HSO_3^{-1} \rightleftharpoons H^+ + SO_3^{-2} \qquad (12)$$

The equilibrium constant is 5.07x 10^{-7} In the experimental range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. During the course of reaction fraction order obtain is 0.16 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz (2008)[19]. Bigelow et al (1898)[4] studied the effect of alcohols on the reactions between sodium sulphite and O_2 and found that the alcohols inhibited the reaction rate. Alyea et al(1929)[1] studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Backstrom (1934)[2] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2. Grgic et al (1998)[10], studied the inhibition effect of acetate, oxlate, format on Fe- catalysed autoxidation of S (IV) at pH 2.8, 3.7,4.5 and found that oxlate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe^{+3} due to formation of complexion with oxlate. Bostjan et al (2006)[13] studied the effect of carboxylic acid on Mn (II) catalysed oxidation of S (IV) and found that mono carboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag (I) catalysed reaction is decelerated by the addition of aniline in the present study. Gupta et al (2008)[14] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3 - 10^4 In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S (IV) by aniline are found to be 1.86 x 10^3 mol dm^{-3} and 0.26 x 10^3 mol dm^{-3} respectively. These values are in the same range as reported by Gupta et al. This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick and Zhang (1996)[7]

$$HSO_3^{-1} \xrightleftharpoons{K_d} H^+ + SO_3^{-2} \quad K_d = 5.01 \times 10^{-7,\,21} \qquad (13)$$

$$Ag^+ + {}^-O_2CCH_3 \xrightleftharpoons{K_{oAc}} AgO_2CCH_3 \quad K_{oAc} = 2.29^{33} \qquad (14)$$

$$Ag^+ + SO_3^{-2} \xrightleftharpoons{K_1} AgOSO_2^- \quad K_1 = 2.51 \times 10^{5},^{39} \qquad (15)$$

$$Ag^+ + HSO_3^{-1} \xrightleftharpoons{K_2} AgHSO_3 \qquad (16)$$

$$AgOSO_2^- + O_2 \xrightleftharpoons{K_3} AgOSO_2^{-1}.O_2 \qquad (17)$$

$$AgHSO_3 + O_2 \xrightleftharpoons{K_4} AgHSO_3.O_2 \qquad (18)$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (19)$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \qquad (20)$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \qquad (21)$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \qquad (22)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \qquad (23)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \qquad (24)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \qquad (25)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \qquad (26)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \qquad (27)$$

$$SO_4^{-\bullet} + \text{Aniline} \xrightarrow{k_{10}} \text{Non Chain product} \qquad (28)$$

By assuming long chain hypothesis and steady state approximation $d[SO_3^{-\bullet}]/dt$, $d[SO_4^{-\bullet}]/dt$, $d[SO_5^{-\bullet}]/dt$, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 29)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Aniline}]\}\,[SO_4^{-1}] \qquad (29)$$

Since the reaction is completely stopped in the presence of [Aniline] at 3×10^{-3} mol dm^{-3}, so the step (22) and (25) appear to be unimportant. The step (24) is ignored because the reaction is completely seized in the presence of higher concentration of aniline by omission and substitution from the above mechanism the following rate law can be obtain (30)

$$R_{cat} = k_1 [Ag(I)] [S(IV)] \ / \ \{k_9[x] + k_{10} [Aniline]\} \qquad (30)$$

Prasad et al (2013)[34] and Gupta et al (2008)[15] proposed a similar mechanism for the Co_2O_3 and CoO catalysed autoxidation of SO_2 inhibited by formic acid and ethanol respectively, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 1.86×10^3 mol dm^{-3} which is in the range of 10^3 - 10^4 and also coincide with the reported value of B of Co_2O_3 catalysed autoxidation of S(IV) by formic acid is 3.58×10^3 mol dm^{-3} So on the basis of calculated value of B we concluded that aniline act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

CONCLUSIONS

The following conclusions are deduced from the results of the aniline inhibited Ag (I) catalysed autoxidation of S(IV) was that inhibit the oxidation with the very slow influence. The value of Inhibition factor of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are in the range of 10^3 -10^4 which shows that free radical mechanism is operative.

REFERENCES

1. Alyea H. N. and Backstrom, H. L. J., (1929), The inhibitive action of alcohols on the autoxidation of sodium sulfite. *Journal of American Chemical Society,* **51**, 90-107.
2. Backstrom H. L. J., (1934), The chain mechanism of the autoxidation of sodium sulfite solutions, *J. Phys. Chem.*(B), **25**, 122-138.
3. Berglund J., Elding L.J., (1995), Manganese-catalysed autoxidation of dissolved sulfur dioxide in the atmospheric aqueous phase. *Atmos. Environ,*. **29**, 1379–1391.
4. Bigelow S. L., (1988), Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.
5. Brandt C., Van Eldik R. , (1995) , Transition metal-catalyzed oxidation of S(IV) oxides, Atmospheric relevant processes and mechanisms. *Chem. Rev,* **95**, 119–180.
6. Coichev N., Van Eldik R., (1994), Metal catalyzed atmospheric reactions, A challenge to coordination chemists. *New J. Chem.,* **18**, 123–131.
7. Connick R.E., Zhang Y-X, Lee S., Adamic R., Chieng P.,(1995), kinetics and mechanism of the oxidation of HSO_3 by O_2, the uncatalyzed reaction. *Inorganic Chemistry,* **34**, 4543–4553.
8. Graedel, T.E., Weschler, C.J., Mandich, M.J.: (1985) Influence of transition metal complexes on atmospheric droplet activity. Nature. 317, 240–242.
9. Grgic I., Dovzan A., Bercic G., Hudnik V., (1998), the effect of atmospheric organic compounds on the Fe catalyzed S(IV) autoxidation in aqueous solution, *J. Atmos. Chem.,* **29**, 315–337.
10. Grgic I., Hudnik V., Bizjak M., Levec J., (1991), Aqueous S(IV) oxidation, catalytic effect of some metals, *Atmos. Environ.,* **25A**, 1591–1597.
11. Grgic I., Hudnik V., Bizjak M., Levec J., (1992) , Aqueous S(IV) oxidation, Synergistic effect of some metal ions. Atmos. Environ. 26A, 571–577.
12. Grgic I., Podkrajsek B., Tursic J., (2002), Influence of pH and organics on autoxidation of S(IV) catalysed by manganese. In Midgeley, P.M., Reuther, M. (eds.) Proceedings from the EUROTRAC-2 Symposium 2002.

13. Grgic I., Poznic M., Bizjak M., (1999) , S(IV) autoxidation in atmospheric liquid water the role of Fe(II) and the effect of oxalate. *J. Atmos. Chem.*, **33**, 89–102.
14. Gupta K.S., Manoj S.V., Mudgak P.K., Sreedharan (2008), Kinetic of iron(III) catalysed autoxidation of S(IV) in acetate buffered medium, *transition metal chem.*, **33**, 3111-316.
15. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., (2008) Kinetics of uninhibited and ethanol inhibited CoO, Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Trans. metal chem.*, **33**, 809-817 doi 10.1007/s 11243-008-9115-6.
16. Ibusuki T., Barnes H.M., (1984), Manganese(II) catalyzed sulfur dioxide oxidation in aqueous solutions at environmental reaction conditions. *Atmos. Environ.*, **18**, 145–151.
17. Ibusuki T., Ohsawa M., (1990), Metal ion catalyzed oxidation of SO_2 in the presence of trace H_2O_2 in aqueous solution under environmental reaction conditions, *Atmos. Environ.*, **24A**, 1325–1330.
18. Ibusuki T., Takeuchi K., (1987), Sulfur dioxide oxidation by oxygen catalyzed by mixture of manganese(II) and iron(III) in aqueous solutions at environmental reaction conditions, *Atmos. Environ.*, **21**, 1555–1560.
19. Irena Wilkosz, Anna Mainka, (2008), Mn(II) catalysed and its inhibition by acetic acid in aq. Phase, *J of atom chem.*, 60,1-17.
20. Kraft J., Van Eldik R., (1989), Kinetics and mechanism of the iron(III) catalyzed autoxidation of S(IV) oxides in aqueous solution, Formation of transient iron(III) – sulphur(IV) complex, *Inorg. Chem.*, **28**, 2297–2305.
21. L.G. Sillen and A.E. Martell, (1964), stability constants of metal ion complex special publication no 17, The Chemical Soc. Burlington house London.
22. Martin L.R., Hill M.W., Tai A.F., Good T., (1991), The iron catalyzed oxidation of sulfur(IV) in aqueous solution, Differing effects of organics at high and low pH. , *J. Geophys. Res.* **96(D2)**, 3085–3097.

23. Martin L.R., Hill M.W., (1987), The effect of ionic strength on the manganese catalyzed oxidation of sulfur (IV). *Atmos. Environ.,* **21**, 2267–2270.
24. Martin L.R., (1984), Kinetic studies of sulphite oxidation in aqueous solution, Calvert, J.G. (ed.) SO_2, NO and NO_2 Oxidation Mechanisms, Atmospheric Considerations. Butterworth, Boston, MA.
25. Novic M., Grgic I., Poje, M., Hudnik V., (1996), Iron-catalyzed oxidation of S(IV) species by oxygen in aqueous solution, influence of pH on the redox cycling of iron. *Atmos. Environ.,* **30**, 4191–4196.
26. Pasiuk-BronikowskaW.Bronikowski, T. Ulejczyk M.,(1997), Solubilization of organics in water coupled with sulphite autoxidation, *Water Res,.* **31**, 1767–1775.
27. Pasiuk-Bronikowska W. Bronikowski, T. Ulejczyk, M., (2003), Inhibition of the S(IV) autoxidation in the atmosphere by secondary terpenic compounds, *J. Atmos. Chem.,* **44**, 97–111.
28. Pasiuk-Bronikowska, W., Bronikowski, T., Ulejczyk, M.: (2003b) Synergy in the autoxidation of S(IV) inhibited by phenolic compounds. J. Phys. Chem. A. 107, 1742–1748.
29. Pasiuk-Bronikowska W., Bronikowski T., (1981), The rate equation for SO_2 autoxidation in aqueous $MnSO_4$ solution containing H_2SO_4, *Chem. Eng. Sci.,* **36**, 215–219.
30. Penkett S.A., Jones B.M.R., Eggleton, A.E.J., (1979), A study of SO_2 oxidation in stored rainwater samplers, *Atmos. Environ.,* **13**, 139–147.
31. Podkrajsek B., Bercic G., Tursic J., Grgic I., (2004), Aqueous oxidation of sulfur(IV) catalyzed by manganese(II) a generalized simple kinetic model, *J. Atmos. Chem.,* **47**, 287–303.
32. Podkrajsek B., Grgic I., Tursic J., Bercic G., (2006), Influence of atmospheric carboxylic acids on catalytic oxidation of sulfur(IV), *J. Atmos. Chem,.* **54**, 103–120.
33. R. Van Eldik, and G,M. Harris, (1980), *Inorg Chem.* **19**, 880.

34. Sameena Begam, Faiyaz Huusain, D.S.N. Prasad, (2013), Kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Pelagia research library*, **4(1)**, 122-131.
35. Sedlak D., Hoigne J., (1993), The role of copper and oxalate in the redox cycling of iron in atmospheric waters, *Atmos. Environ.*, **27A**, 2173–2185.
36. Seigneur C., Saxena P., (1984), A study of atmospheric acid formation in different environments, *Atmos. Environ,*.**18**, 2109–2124.
37. Seinfeld J.H., Pandis S.N., (1998), Atmospheric Chemistry and Physics. From Air Pollution to Climate Change, Wiley New York.
38. Tursic J., Grgic I., Podkrajsek B., (2003), Influence of ionic strength on aqueous oxidation of SO_2 catalyzed by manganese, *Atmos. Environ.*, **37**, 2589–2595.
39. V.F. Toropova I.A. Sirotina and V.B. Rotanova,(1955), Uchenye Zapiski Kazanskogo Uni., 115 no.3, 53.
40. Wolf A., Deutsch F., Hoffmann P., Ortner H.M., (2000), The influence of oxalate on Fe-catalyzed S(IV) oxidation by oxygen in aqueous solutions, *J. Atmos. Chem.*, **37**, 125–13.
41. Ziajka J., Pasiuk-Bronikowska W., (2003), Autoxidation of sulphur dioxide in the presence of alcohols under conditions related to the tropospheric aqueous phase, *Atmos. Environ.*, **37**, 3913–3922.
42. Ziajka J., Pasiuk-Bronikowska W.,(2008), Rate constants for atmospheric trace organic scavenging SO_4^- in the Fe - catalysed autoxidation of S(IV), *Atmos. Environ.*, **39**, 1431–1438.

CHAPTER - VIII

Kinetics of Benzamide Inhibited Uncatalysed and Ag (I) Catalysed Autoxidation of S (IV) in Acidic Medium

ABSTRACT

The kinetics of atmospheric autoxidation of S(IV) by Ag (I) in the pH range 4.02-5.25 has been studied. Based on the observed results a free radical mechanism operative and following rate law has been proposed.

$-d\,[S(IV)/dt \quad = \quad (k_1+k_2[Ag])\,[S(IV)]/\,1 + \; B\,[Benzamide]$

INTRODUCTION

The aqueous phase oxidation of dissolved sulfur dioxide by atmospheric oxidants, i.e., oxygen, ozone, and hydrogen peroxide, is a major cause of rainwater acidity (Brandt and van Eldik 1995[5], Rodhe et al. 2002[30], Gupta 2012[11]). The oxidation of dissolved SO_2 by O_2 is known to be slow, but the trace metal ions, particularly of transition variety, catalyzes this reaction strongly (Martin 1984) [25]. To understand the nature of the catalysis and its mechanism, the effect of environmentally important metal ions such as Fe(II)/ (III) (Martin et al. 1991[25], Manoj et al. 2008)[23], Co(II/III) (Gupta et al. 2008)[12], Cu(II) (Sharma et al. 2011[32] Prasad et al. 1992[28], Grgic et al. 1991[10], Jain et al. 1995)[17] Mn(II)/(III) (Huss et al. 1982[15], Connick and Zhang 1996[9], Coichev and van Eldik 1991[7] and Ni(II) (Linn et al. 1990[20], Sharma et al. 2011)[32] on the oxidation of dissolved SO_2, here in after referred to as S(IV), has been studied under a variety of reaction conditions.

In aqueous atmospheric systems and in the absence of any added substance from outside, S(IV) autoxidation is believed to operate via a radical mechanism involving oxysulfur radicals, viz., $SO_3^{-\bullet}$; $SO_4^{-\bullet}$,and $SO_5^{-\bullet}$as evidenced by the inhibiting action of free radical scavengers (Brandt and van Eldik 1995)[5], Ammonia and ammonium ions also inhibit the reaction analogously (Mudgal et al. 2008)[26]. Among the inhibitors, volatile organic compounds (VOCs) have been found to be strong inhibitors of S(IV) autoxidation (Lunak et al. 1978[21] Connick et al. 1995[9], Connick and Zhang 1996[8], Ziajka and Pasiuk-Bronikowska 2003[34], Huss et al. 1982[15], Manoj et al. 1999[24], 2008[23] Gupta et al. 2008[12], Alyea and Backstrom 1929)[1]. The realization of importance of the role of organic compounds in atmospheric chemistry of smog, stratospheric ozone depletion, hydroxyl radical reactions etc., has led to the measurement of organics in atmosphere, and a large amount of data has accumulated (Hester et al. 1995)[14]. There have been several studies on the identification and measurement of volatile organic compounds in air (Hester et al. 1995)[14]. The organic compounds in rainwater have also been detected and measured (Okochi et al. 2005[27], Manabu et al. 1999[22], Avery et al. 2009)[2]. A large number of VOCs such as alcohols, aromatic hydrocarbons and aliphatic chloro derivatives have been detected and determined in atmospheric waters globally. Okochi et al. (2005)[27] have reported measurable amounts of benzene, toluene, xylene, and other compounds in rainwater. In Brazil, several studies have found significant amounts of ethanol (Campos et al. 2007)[6], which is a known strong inhibitor of [S(IV)] autoxidation. The effect of aromatic amides i.e. benzamide in atmospheric water on the transition metal-catalysed oxidation of S(IV) is not fully known yet and more work in this area is needed to understand these processes better. The purpose of the present study was to study the kinetics of the Ag(I) catalysed S(IV) oxidation and to determine the inhibiting effect of benzamide on this process under different experimental conditions.

EXPERIMENTAL

The experimental procedure was exactly the same as described earlier.[31] All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature $30\underline{+}1^0$ C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at $1600\underline{+}10$ rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreached S(IV) iodometrically. The reproducibility of replicate measurements was generally better than $10\underline{+}1$ %. All calculations were performed in MS Excel.

PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S(VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure.

The product analysis showed the recovery of sulphate to be 98±1%. in all cases in agreement with eq. (1)

$$S(IV) + 0.5\,O_2 \longrightarrow S\,(VI) \qquad (1)$$

RESULTS

Preliminary Investigation

The kinetics of both uncatalysed and Ag (I) catalysed and benzamide inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30 ^{o}C. In both the cases the first order dependence of S(IV) was observed in the kinetics data treatment for the determination of first order rate constant k_1 was carried out from log [S(IV)] versus time, t. The plots were shown in fig.8.1 from the fig.8.1 observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by benzamide.

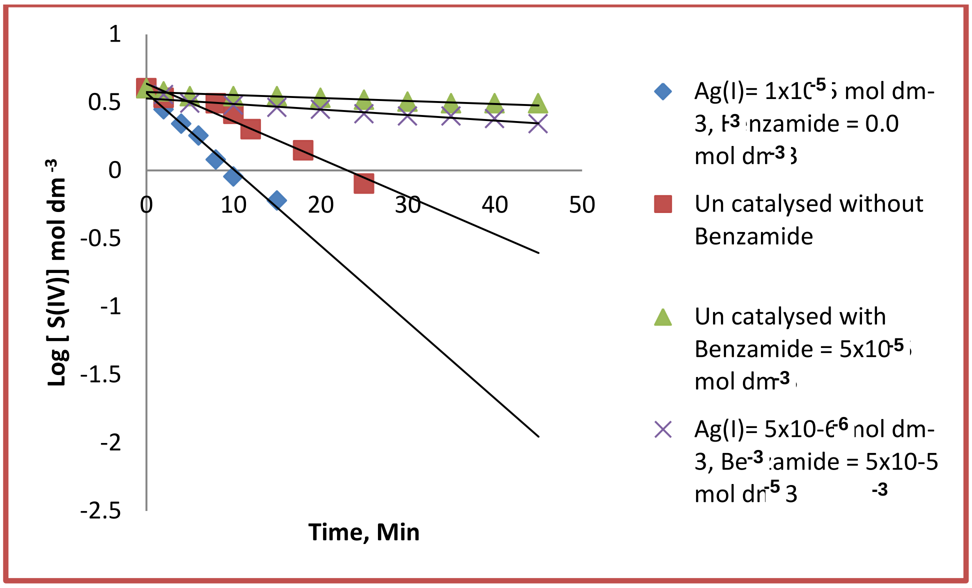


Fig. 8.1: The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] =2 x 10^{-3} mol dm^{-3} at pH = 4.95, t = 30^{o} C.

(◇) Ag (I) = 1x 10^{-5} mol dm^{-3}, [Benzamide] = 0.0 mol dm^{-3}

(□) Uncatalysed without benzamide

(△) Uncatalysed with [Benzamide] = 5x10^{-5} mol dm^{-3}

(x) Ag (I) = 5x 10^{-6} mol dm^{-3}, [Benzamide] = 5x 10^{-5} mol dm^{-3}

Uncatalysed Reaction

Uncatalysed reaction was studied in the absence of Ag (I) and all the solutions were prepared in doubly distilled water.

Table- 8.1

Quantitative Analysis of Sulphate in Final Product Solution

10^3 [S(IV)] mol dm^{-3}	Ag (I) mol dm^{-3}	pH	10^3 [SO_4^{-2}] mol dm^{-3}	[SO_4^{-2}] /[S(IV)]	%of S(IV) recovery
5.0	0.00	4.95	4.90	0.980	98.0
5.0	$5x10^{-6}$	4.95	4.92	0.984	98.4
5.0	$1x10^{-5}$	4.95	4.95	0.990	99.0

Table- 8.2

Variation of [S (IV)] at pH = 4.95, t = 30⁰ C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	3	4
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot			
(0)	0.0	0.0	0.0	0.0
(2)	0.5	0.6	1.3	1.6
(8)	0.8	0.9	2.1	2.2
(10)	1.0	1.4	3.2	3.2
(12)	1.2	2.0	3.8	4.3
(18)	1.4	2.6	4.6	5.4
(25)	1.6	3.2	4.8	6.5
∞	2.0	4.0	6.0	8.0
(10^3) k_1 s^{-1}	**1.04**	**1.06**	**1.09**	**1.09**

Figures in parentheses denotes time in minutes

Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range from $1x10^{-3}$ mol dm^{-3} to $4x10^{-3}$ mol dm^{-3} at pH = 4.95, t = 30^{o} C in acetate buffered medium. The kinetics was found to be first order in [S(IV)] and values of k_1 was calculated from log [S(IV)] v/s time plots which was linear. The value of first order rate constant k_1 are given in table - 8.3, the dependence of reaction rate on [S(IV)] follows the rate law (2)

$$-d\,[S(IV)]\,/dt \quad = \quad k_1\,[S(IV)] \qquad (2)$$

Table- 8.3

The values of k_1 for uncatalysed reaction at different [S(IV)], pH = 4.95, t = 30^{o} C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH= 3x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	**$(10^{3})\ k_1\ s^{-1}$**
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

[Benzamide] Dependence

The major aim of this study was to examine the effect of benzamide on the autoxidation of S(IV) in acetate buffer medium and varying the [Benzamide] from $1x10^{-8}$ mol dm^{-3} to $5x10^{-5}$ mol dm^{-3}, we observed the rate of the reaction decreased by increasing [Benzamide]. The results are given in table 8.4 However the nature of the [S(IV)] dependence in presence of benzamide did not change and remains first order. The first order rate constant k_{inh} in the presence of benzamide was defined by rate law (3)

$$-d\,[S(IV)]\,/dt \quad = \quad k_{inh}\,[S(IV)] \qquad (3)$$

The values of k_{inh} in the presence of benzamide decreased with increasing [Benzamide] are given in table 8.5 which are in agreement with the rate law (4)

$$k_{inh} \;=\; k_1\,/\,(1+B\,[Benzamide]) \qquad (4)$$

Where B is inhibition parameter for rate inhibition by benzamide

The equation (4) on rearrangement becomes

$$1/\,k_{inh} \;=\; 1/\,k_1 + B\,[Benzamide]\,/\,k_1 \qquad (5)$$

In accordance with the equation (5) the plot of 1/ k_{inh} v/s [Benzamide] was found to be linear with non- zero intercept fig 8.2 The values of intercept (1/ k_1) and slope (B/ k_1) were found to be1.68 x 10^3 s and 8.07 x 10^7 mol dm^{-3} s at pH = 4.95, t = 30^o C from these values the value of inhibition parameter B was found to be 4.78 x 10^4 mol dm^{-3}

Table-8.4

Variation of [Benzamide], at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C,
CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH= $3x10^{-2}$ mol L^{-1}

[Benzamide] mol dm^{-3}	**$1x10^{-8}$**	**$5x10^{-8}$**	**$8x10^{-8}$**	**$2x10^{-7}$**	**$5x10^{-7}$**	**$7x10^{-7}$**	**$3x10^{-6}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot									
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.5	0.4	0.5	0.5	0.4	0.4	0.3	0.4
(5)	0.9	0.8	0.8	0.6	0.9	0.7	0.6	0.7	0.5	0.9
(10)	1.3	1.1	1.1	1.0	1.3	0.9	0.9	0.9	0.9	1.0
(15)	1.7	1.3	1.3	1.2	1.5	1.2	1.1	1.1	1.0	1.1
(20)	2.1	1.5	1.5	1.5	1.7	1.5	1.3	1.3	1.3	1.2
(25)	2.4	1.9	1.9	1.8	2.0	2.0	1.9	1.5	1.4	1.4
(30)	2.8	2.2	2.5	2.2	2.2	2.2	2.2	2.0	1.8	1.5
(35)	3.1	2.5	2.9	2.5	2.6	2.3	2.5	2.3	2.0	1.5
(40)	3.3	3.3	3.3	2.9	2.9	2.9	2.9	2.8	2.1	1.6
(45)	3.5	3.6	3.4	3.5	3.5	3.4	3.1	3.0	2.3	1.8
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.728**	**0.697**	**0.672**	**0.613**	**0.597**	**0.569**	**0.521**	**0.464**	**0.303**	**0.18**

Figures in parentheses denotes time in minute

Table- 8.5

The values of k_{inh} at different [Benzamide], pH = 4.95, t = 30° C

$CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH= 3x10^{-2}$ mol L^{-1}

[Benzamide] mol dm^{-3}	10^3 k_{inh} s^{-1}	$1/k_{inh}$ s
$1.0x10^{-8}$	0.728	1374
$5.0x10^{-7}$	0.697	1435
$8.0x10^{-7}$	0.672	1488
$2.0x10^{-6}$	0.613	1631
$5.0x10^{-6}$	0.597	1675
$7.0x10^{-6}$	0.569	1757
$3.0x10^{-5}$	0.521	1919
$5.0x10^{-5}$	0.464	2155
$8.0x10^{-5}$	0.303	3300
$5.0x10^{-3}$	0.180	5555

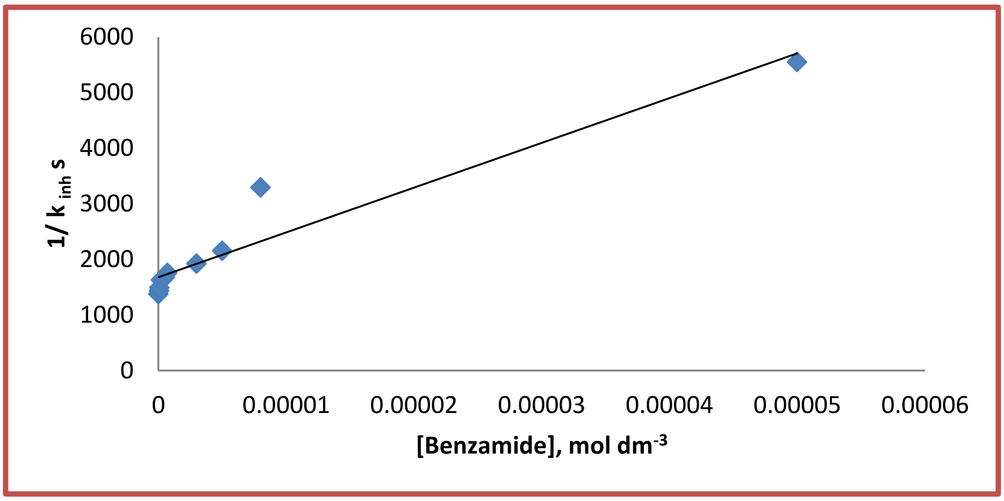


Fig. 8.2: Effect of benzamide at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30° C, in acetate buffered medium.

Ag(I) Catalysed Reaction

At first the kinetics of Ag(I) Catalysed reaction in the absence of inhibitor was studied.

[S(IV)] Variation

The dependence of S (IV) on reaction rate was studied by varying [S(IV)] from $1\text{x}10^{-3}$ mol dm^{-3} to $10\text{x}10^{-3}$ mol dm^{-3} at two different but fixed Ag(I) of $5\text{x}10^{-6}$ mol dm^{-3} and $1\text{x}10^{-5}$ mol dm^{-3} at pH = 4.95, t = 30^{o} C. The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in fig 8.1

Ag(I) variations

The dependence of Ag(I) on the reaction rate was studied by varying Ag (I) from $5\text{x}10^{-6}$ mol dm^{-3} to $2.5\text{x}10^{-5}$ mol dm^{-3} at S(IV) = $2\text{x}10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig 8.3. The nature of dependence of k_{cat} on Ag(I) was indicated as two term rate law – (6)

$$-d\,[S(IV)]\,/dt \quad = \quad k_{cat}\,[S(IV)] \; = (k_1+k_2[Ag(I)]\,[S(IV)] \qquad (6)$$

$$\text{Or}\;\; k_{cat}= \;\; k_1+k[Ag(I)] \qquad (7)$$

From the plot in fig 8.3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be $0.72\text{x}\ 10^{1}$ s and $8.6\ \text{x}\ 10^{-3}$ mol dm^{-3} respectively at pH = 4.95, t = 30^{o} C in acetate buffered medium.

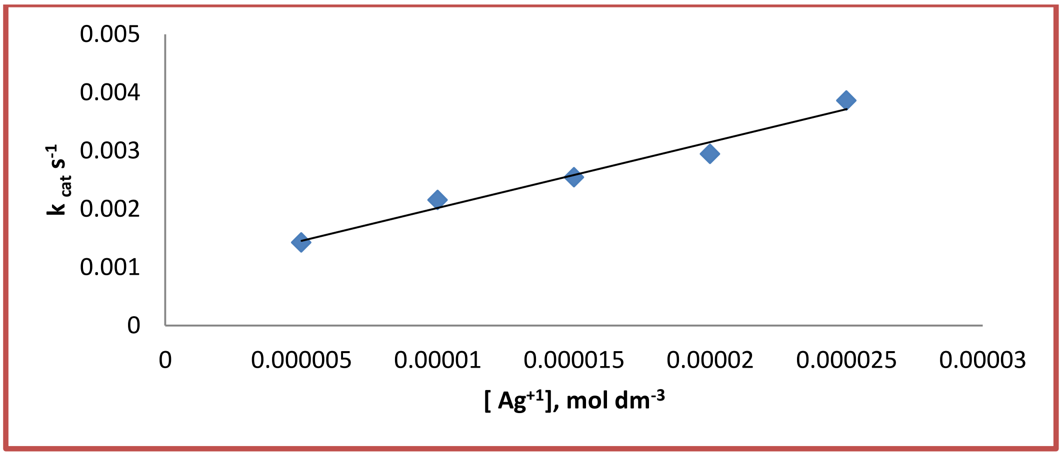


Fig. 8.3: The dependence of catalyst concentration at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium.

Table- 8.6

Variation of [S(IV)] = $2x10^{-3}$ mol dm^{-3} at Ag (I) = $5x10^{-6}$ mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.2	0.4	0.8	1.5	2.0	2.2
(4)	0.4	1.0	1.7	2.4	3.3	4.5
(6)	0.6	1.2	2.7	3.0	4.5	6.5
(8)	0.9	1.5	3.6	4.0	7.0	9.8
(10)	1.2	1.7	5.0	5.5	9.3	12.1
(15)	1.4	3.0	5.5	9.0	11.5	14.4
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.43**	**1.42**	**1.41**	**1.44**	**1.46**	**1.50**

Figures in parentheses denotes time in minutes.

Table- 8.7

Variation of [S(IV)] = 2x10^{-3} mol dm^{-3} at Ag (I) =1x10^{-5} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

10^{3} [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.9	3.0	4.5	5.6
(4)	0.8	1.8	2.8	4.8	6.3	7.8
(6)	1.2	2.2	3.6	5.9	7.8	9.5
(8)	1.4	2.8	4.5	7.8	8.9	10.2
(10)	1.5	3.1	5.0	8.9	12.5	12.8
(15)	1.7	3.4	7.0	10.3	13.6	17.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^{3}) k_1 s^{-1}	**2.19**	**2.15**	**2.15**	**2.18**	**2.14**	**2.10**

Figures in parentheses denotes time in minutes.

Table-8.8

Variation of Ag (I) at [S(IV)] = $2x10^{-3}$ mol dm^{-3} pH = 4.95, t = 30^{o} C, $CH_3COONa = 7x10^{-2}$ mol L^{-1}, $CH_3COOH = 3x10^{-2}$ mol L^{-1}

Ag (I) mol dm^{-3}	**$5x10^{-6}$**	**$1x10^{-5}$**	**$1.5x10^{-5}$**	**$2x10^{-5}$**	**$2.5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	1.2	1.4	2.5	2.4
(4)	1.0	1.8	1.8	2.7	2.5
(6)	1.2	2.2	2.0	2.9	3.0
(8)	1.5	2.8	2.2	3.7	3.5
(10)	1.7	3.1	3.4		
(15)	3.0	3.4			
∞	4.0	4.0	4.0	4.0	4.0
$(10^{3})\ k_1\ s^{-1}$	**1.42**	**2.15**	**2.54**	**2.94**	**3.88**

Figures in parentheses denotes time in minutes.

Table - 8.9

The values of k_{cat} at different concentration of Ag (I) mol dm^{-3}, pH = 4.95, t = 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	10^3 k_{cat} s^{-1}
0.000005	1.42
0.00001	2.15
0.00015	2.54
0.00020	2.94
0.00025	3.88

Variation of pH

Variation of pH was carried out from 4.02-5.25 at different [S(IV), Ag (I), [Benzamide] and temperatures. The rate decreases slightly by varying pH is inverse H^+ ion dependence was observed. From the plot of log k_1 v/s log (H^+) the order with respect to H^+ is 0.23 which is a fractional order and can be neglected as shown in fig 8.4.

Table - 8.10

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Benzamide] = 7.0x10^{-7}mol dm^{-3}, t= 30^o C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	10 ^{3} ks^{-1}
4.02	0.489
4.35	0.559
4.56	0.627
4.75	0.714
4.95	0.842
5.25	0.901

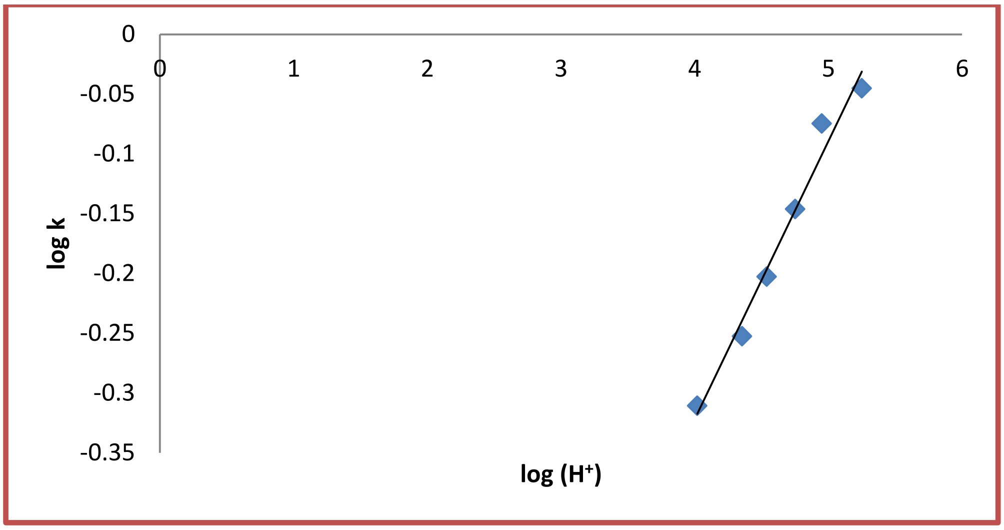


Fig. 8.4: Effect of pH at [S(IV)] = 2x10^{-3} mol dm^{-3} Ag (I) = 5x10^{-6} mol dm^{-3}, [Benzamide] = 7.0x10^{-7} mol dm^{-3}, t= 30° C in acetate buffered medium.

Table - 8.11

Rate of Ag (I) Catalysed Autoxidation in the Presence of Benzamide.

[Benzamide], mol dm^{-3}	Ag (I) =5x10^{-6} mol dm^{-3}	Ag (I) =1 x 10^{-5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.02			
7.0 x 10^{-7}	0.489 x 10^{-3}	0.627 x 10^{-3}	0.901 x 10^{-3}
7.0x 10^{-6}	0.316 x 10^{-3}	_	_
8.0 x 10^{-5}	0.248 x 10^{-3}	_	_
pH = 4.50			
7.0 x 10^{-7}	0.513 x 10^{-3}	0.703 x 10^{-3}	1.15 x 10^{-3}
7.0x 10^{-6}	0.478 x 10^{-3}	_	_
8.0 x 10^{-5}	0.419 x 10^{-3}	_	_
pH = 5.25			
7.0 x 10^{-7}	0.653 x 10^{-3}	0.733x 10^{-3}	1.39 x 10^{-3}
7.0x 10^{-6}	0.625 x 10^{-3}	_	_
8.0 x 10^{-5}	0.544 x 10^{-3}	_	_

Table - 8.12

Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of benzamide.

[Benzamide] =7.0 x 10^{-7} mol dm^{-3}	Ag (I) =5x10^{-6} mol dm^{-3}	Ag (I) =1 x 10^{-5} mol dm^{-3}	Ag (I) =1.5 x 10^{-5} mol dm^{-3}
pH = 4.50			
	2.90	**3.43**	**2.82**

Table - 8.13

Variation of pH at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3} [Benzamide] = 7x10^{-7} mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.5	0.5	0.5	0.5	0.6
(5)	0.6	0.8	0.7	0.8	0.8	0.9
(10)	0.9	1.1	0.9	1.3	1.5	1.3
(15)	1.3	1.5	1.2	1.5	1.9	1.5
(20)	1.6	1.8	1.5	1.7	2.3	1.9
(25)	1.9	2.2	1.8	1.9	2.5	2.2
(30)	2.2	2.5	2.5	2.5	3.0	2.9
(35)	2.5	2.9	2.9	2.9	3.3	3.2
(40)	2.8	3.0	3.1	3.4	3.5	3.6
(45)	3.0	3.1	3.3	3.5	3.6	3.7
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1, s^{-1}	**0.489**	**0.559**	**0.627**	**0.714**	**0.842**	**0.901**

Figures in parentheses denotes time in minutes.

Table - 8.14

Variation of pH at [S(IV)] = $4x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3} [Benzamide] = $7x10^{-7}$ mol dm^{-3}, t= 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.9	1.0	1.1	1.2	1.2	1.2
(5)	1.3	1.8	1.9	1.9	2.0	2.2
(10)	1.9	2.8	2.4	2.4	2.4	2.9
(15)	2.6	3.5	3.0	2.9	3.0	3.4
(20)	2.9	4.2	3.4	3.4	3.6	4.0
(25)	3.3	5	3.6	4.3	4.3	4.4
(30)	3.6	5.3	4.9	5.3	5.5	5.6
(35)	4.8	5.9	5.6	6.2	6.3	6.4
(40)	5.7	6.3	6.4	6.8	7.2	7.3
(45)	6.4	6.4	6.9	7.0	7.3	7.5
∞	8.0	8.0	8.0	8.0	8.0	8.0
(10^3) k_1, s^{-1}	**0.504**	**0.600**	**0.644**	**0.739**	**0.859**	**0.928**

Figures in parentheses denotes time in minutes.

Table - 8.15

Variation of pH at [S(IV)] = 6x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, [Benzamide] = 7x10^{-7} mol dm^{-3}, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	1.5	1.7	1.4	1.5	1.6	1.5
(5)	2.3	2.5	2.6	2.7	2.7	2.4
(10)	3.1	3.3	3.5	3.5	3.8	3.8
(15)	4.4	4.5	4.3	4.3	4.5	4.4
(20)	5.7	5.8	5.9	5.6	5.9	5.8
(25)	6.7	6.8	6.5	6.2	6.5	6.4
(30)	7.3	7.5	7.2	7.5	7.7	7.7
(35)	8.1	8.2	8.9	8.8	9.0	8.9
(40)	8.6	9.1	9.5	9.9	10.3	10.6
(45)	9.1	10.2	10.3	10.9	11.3	11.5
∞	12.0	12.0	12.0	12.0	12.0	12.0
(10^3) k_1, s^{-1}	**0.515**	**0.614**	**0.659**	**0.751**	**0.860**	**0.943**

Figures in parentheses denotes time in minutes.

Table - 8.16

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $1x10^{-5}$ mol dm^{-3} [Benzamide] = $7x10^{-7}$mol dm^{-3}, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10 $^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.5	0.6	0.6	0.8	0.8
(5)	0.7	0.8	0.8	1.2	1.2	1.3
(10)	0.9	1.2	1.1	1.6	1.6	1.6
(15)	1.4	1.5	1.4	1.8	2.0	2.1
(20)	1.6	1.8	1.6	2.2	2.4	2.5
(25)	1.9	2.3	2.2	2.6	2.8	2.9
(30)	2.4	2.5	2.8	3.0	3.3	3.6
(35)	2.8	2.9	3.3	3.3	3.6	3.7
∞	4.0	4.0	4.0	4.0	4.0	4.0
$(10^{3})k_1, s^{-1}$	**0.513**	**0.560**	**0.703**	**0.749**	**1.00**	**1.15**

Figures in parentheses denotes time in minutes.

Table - 8.17

Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) = 1.5×10^{-5} mol dm^{-3}, [Benzamide] = 7×10^{-7}mol dm^{-3}, t= 30^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.8	0.9	0.9	0.8
(5)	0.8	0.8	1.1	1.3	1.3	1.2
(10)	1.0	1.2	1.3	1.5	1.6	1.6
(15)	1.3	1.6	1.5	1.9	2.5	2.0
(20)	1.5	2.0	1.8	2.5	2.9	2.5
(25)	2.0	2.3	2.2	2.9	3.2	2.9
(30)	2.4	2.6	2.6	3.2	3.5	3.8
(35)	3.0	3.0	3.5	3.3	3.8	3.8
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.552**	**0.602**	**0.733**	**0.811**	**1.26**	**1.39**

Figures in parentheses denotes time in minutes.

Table - 8.18

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Benzamide] = $7x10^{-6}$ mol dm^{-3}, t= 30^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol cm^{-3} Hypo for 5 ml aliquot					
0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.4	0.6	0.7	0.8	0.8	0.8
(10)	0.5	0.9	0.9	1.3	1.2	1.2
(15)	0.7	1.3	1.2	1.5	1.5	1.4
(20)	1.0	1.7	1.4	1.8	1.9	1.8
(25)	1.3	2.2	1.6	2.2	2.2	2.0
(30)	1.4	2.4	1.8	2.4	2.3	2.3
(35)	1.6	2.6	2.2	2.8	2.6	2.5
(40)	1.8	2.6	2.4	3.1	3.0	2.9
(45)	2.3	2.8	2.8	3.2	3.3	3.3
(50)	2.6	3.0	3.3	3.2	3.4	3.5
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.316**	**0.459**	**0.478**	**0.566**	**0.606**	**0.625**

Figures in parentheses denotes time in minutes.

Table - 8.19

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3} Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Benzamide] = $8x10^{-5}$ mol dm^{-3}, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol cm^{-3} Hypo for 5 ml aliquot					
0	0.0	0.0	0.0	0.0	0.0	0.0
(5)	0.3	0.5	0.6	0.5	0.8	0.9
(10)	0.5	0.9	0.9	0.8	1.0	1.5
(15)	0.7	1.3	1.2	1.0	1.3	1.6
(20)	0.9	1.6	1.3	1.3	1.5	1.9
(25)	1.2	2.0	1.5	1.5	1.9	2.2
(30)	1.4	2.5	1.9	2.0	2.1	2.5
(35)	1.5	2.6	2.2	2.2	2.4	2.6
(40)	1.8	2.7	2.4	2.5	2.6	2.8
(50)	2.0	2.8	2.8	2.9	2.9	3.3
(60)	2.4	2.9	3.2	3.2	3.4	3.5
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.248**	**0.394**	**0.419**	**0.443**	**0.475**	**0.544**

Figures in parentheses denotes time in minutes

Table - 8.20

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Benzamide] = $7x10^{-7}$mol dm^{-3}, t= 35^o C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.6	0.5	0.6	0.6	0.6
(5)	0.7	1.0	0.7	0.9	0.9	0.9
(10)	1.0	1.4	0.9	1.4	1.4	1.3
(15)	1.4	1.8	1.3	2.0	1.9	1.6
(20)	1.8	2.2	1.6	2.3	2.3	1.9
(25)	2.0	2.5	2.0	2.6	2.6	2.2
(30)	2.3	2.6	2.3	2.9	3.2	3.0
(35)	2.5	2.9	2.8	3.4	3.4	3.4
(40)	3.0	3.2	3.5	3.4	3.5	3.7
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.508**	**0.608**	**0.681**	**0.794**	**0.867**	**0.934**

Figures in parentheses denotes time in minutes

Table - 8.21

Variation of pH at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = $5x10^{-6}$ mol dm^{-3}, [Benzamide] = $7x10^{-7}$ mol dm^{-3}, t= 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}

pH	**4.02**	**4.35**	**4.56**	**4.75**	**4.95**	**5.25**
Time, (Min)	Volume of 5 $x10^{-3}$ mol cm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.8	0.8	0.8	0.7	0.8
(5)	0.8	1.2	1.1	1.0	0.9	1.2
(10)	1.0	1.6	1.5	1.4	1.4	1.5
(15)	1.4	2.1	1.9	2	1.9	2.0
(20)	1.8	2.4	2.3	2.4	2.4	2.2
(25)	2.1	2.6	2.7	3.0	2.8	3.0
(30)	2.4	3.0	3.0	3.2	3.3	3.5
(35)	2.6	3.1	3.2	3.2	3.5	3.7
(40)	3.3	3.2				
∞	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1, s^{-1}	**0.593**	**0.655**	**0.723**	**0.808**	**0.941**	**1.12**

Figures in parentheses denotes time in minutes

Table- 8.22

Variation of [S(IV)] at Ag (I) = 5 x10^{-6} mol dm^{-3} , [Benzamide] = 7x10^{-7} mol dm^{-3}, pH = 4.95, t = 30^{0} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.3	0.5	0.8	1.9	2.9	3.5
(5)	0.5	0.8	1.6	2.8	3.5	5.2
(10)	0.7	1.5	2.3	3.4	4.9	6.4
(15)	0.9	1.9	3.1	4.2	6.1	7.5
(20)	1.0	2.3	4.2	5.5	7.2	8.9
(25)	1.2	2.5	5.1	6.7	8.5	10.1
(30)	1.3	3.0	6.2	7.5	9.9	12.5
(35)	1.7	3.3	6.8	8.5	11.2	14.5
(40)	1.7	3.5	6.9	9.9	13.2	17.5
(45)	1.8	3.6	7.0	11.3	15.1	18.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.804**	**0.842**	**0.859**	**0.860**	**0.811**	**0.809**

Figures in parentheses denotes time in minutes

Table- 8.23

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$ mol dm^{-3}(Benzamide) =$7x10^{-7}$ mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.3	0.5	0.9	2.1	3.1	3.3
(5)	0.5	0.9	1.6	3.5	4.9	5.1
(10)	0.7	1.5	2.4	4.2	5.9	6.7
(15)	0.9	1.9	3.3	5.1	6.7	7.7
(20)	1.1	2.3	4.5	6.1	7.4	9.1
(25)	1.2	2.5	5.1	7.2	8.8	10.5
(30)	1.4	3.1	6.4	8.2	10.2	12.6
(35)	1.8	3.4	7.1	9.5	12.4	14.7
(40)	1.9	3.8	7.4	11.6	14.6	17.7
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.06**	**1.00**	**1.03**	**1.01**	**1.00**	**1.00**

Figures in parentheses denotes time in minutes

Table - 8.24

Variation of [S(IV)] at Ag (I) =2 x10^{-5} mol dm^{-3}, [Benzamide] = 7x10^{-7} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.7	1.3	2.5	3.4	4.2
(5)	0.8	1.1	2.1	4.6	5.1	6.7
(10)	1.1	1.4	3.2	6.1	7.6	8.8
(15)	1.2	1.9	4.1	7.9	8.5	10.2
(20)	1.4	2.4	5.3	9.1	9.9	12.4
(25)	1.8	3.2	6.5	10.2	11.7	14.5
(30)	1.8	3.7	7.3	10.9	15.2	17.9
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.27**	**1.26**	**1.21**	**1.25**	**1.26**	**1.21**

Figures in parentheses denotes time in minutes

Table- 8.25

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Benzamide] = 7x10^{-7} mol dm^{-3}, pH = 4.95, t = 30 °C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10 $^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.3	0.3	0.4	0.8	0.9
(5)	0.5	0.5	0.8	1.2	1.2
(10)	0.7	0.7	1.1	1.4	1.4
(15)	0.9	0.9	1.2	1.6	1.7
(20)	1.0	1.1	1.7	1.7	1.8
(25)	1.2	1.2	1.8	1.7	1.8
(30)	1.3	1.4	1.8	1.9	1.9
(35)	1.7	1.8	1.8	1.9	1.8
(40)	1.7	1.9			
(45)	1.8				
∞	2.0	2.0	2.0	2.0	2.0
(10 ^{3}) k_1 s^{-1}	**0.804**	**1.06**	**1.21**	**1.32**	**1.50**

Figures in parentheses denotes time in minutes

Table- 8.26

Variation of Ag (I) at S(IV)]= 2 x10^{-3} mol dm^{-3}, [Benzamide] = 7x10^{-7} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.5	0.7	0.9	0.9
(5)	0.8	0.9	1.1	1.3	1.3
(10)	1.5	1.5	1.4	1.4	1.7
(15)	1.9	1.9	1.9	1.7	2.6
(20)	2.3	2.3	2.4	2.6	3.5
(25)	2.5	2.5	3.2	3.5	3.7
(30)	3.0	3.1	3.7	3.7	3.7
(35)	3.3	3.4			
(40)	3.5	3.8			
(45)	3.6				
∞	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.842**	**1.00**	**1.26**	**1.32**	**1.58**

Figures in parentheses denotes time in minutes

Table- 8.27

Variation of Ag (I) at S(IV)]= 4 x10^{-3} mol dm^{-3}, [Benzamide] = 7x10^{-7} mol dm^{-3}, pH = 4.95, t = 30^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.8	1.1	1.4	1.8	1.7
(5)	1.6	2.1	2.1	2.7	2.7
(10)	2.3	3.2	2.9	3.8	3.4
(15)	3.1	4.5	3.5	4.7	4.9
(20)	4.2	5.5	4.5	5.9	6.5
(25)	5.1	6.4	6.2	7.3	7.4
(30)	6.2	7.0	7.5		
(35)	6.8	7.0			
(40)	6.9				
(45)	7.0				
∞	8.0	8.0	8.0	8.0	8.0
(10^{3}) k_1 s^{-1}	**0.859**	**1.03**	**1.21**	**1.38**	**1.58**

Figures in parentheses denotes time in minutes

Table- 8.28

Variation of benzamide at [S(IV)] = $2\text{x}10^{-3}$ mol dm^{-3}, Ag (I) = 5 $\text{x}10^{-6}$ mol dm^{-3}, pH = 4.95, t= 30^{o} C, CH_3COONa = $7\text{x}10^{-2}$ mol L^{-1}, CH_3COOH = $3\text{x}10^{-2}$ mol L^{-1}

[Bezamide] mol dm^{-3}	**$5\text{x}10^{-8}$**	**$8\text{x}10^{-8}$**	**$7\text{x}10^{-7}$**	**$3\text{x}10^{-6}$**	**$5\text{x}10^{-6}$**	**$8\text{x}10^{-6}$**	**$2\text{x}10^{-5}$**	**$5\text{x}10^{-5}$**
Time, (Min)	Volume of 5 $\text{x}10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.6	0.6	0.5	0.5	0.5	0.5	0.5	0.5
(5)	0.9	0.9	0.8	0.8	0.8	0.8	0.8	0.6
(10)	1.5	1.5	1.5	1.0	1.3	1.4	0.9	0.7
(15)	1.9	1.9	1.9	1.3	1.5	1.9	1.0	0.9
(20)	2.4	2.5	2.3	1.5	2.1	2.3	1.3	1.2
(25)	2.9	3.0	2.5	2.0	2.5	2.4	1.5	1.4
(30)	3.2	3.2	3.0	2.5	3.0	2.5	1.9	1.6
(35)	3.5	3.4	3.3	2.9	3.0	2.6	2.2	1.8
(40)			3.5	3.3	3.1	2.6	2.5	1.9
(45)			3.6	3.3	3.1	2.8	2.5	2.0
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.929**	**0.898**	**0.842**	**0.650**	**0.607**	**0.430**	**0.353**	**0.244**

Figures in parentheses denotes time in minutes

Table- 8.29

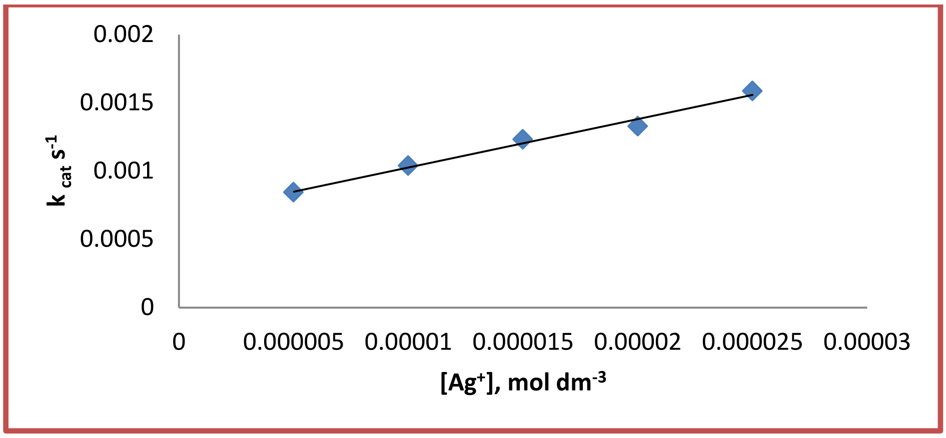
Variation of benzamide at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) =$1x10^{-5}$ mol dm^{-3}, pH = 4.95, t = 30^0 C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

[Bezamide] mol dm^{-3}	**$5x10^{-8}$**	**$8x10^{-8}$**	**$7x10^{-7}$**	**$3x10^{-6}$**	**$5x10^{-6}$**	**$8x10^{-6}$**	**$2x10^{-5}$**	**$5x10^{-5}$**
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.7	0.8	0.6	0.6	0.5	0.5	0.6	0.5
(5)	0.9	1.2	0.8	0.9	0.8	0.8	0.9	0.6
(10)	1.4	1.5	1.4	1.3	1.3	1.5	1.2	0.7
(15)	1.9	1.9	1.9	1.6	1.5	1.9	1.3	0.9
(20)	2.5	2.5	2.4	2.1	2.1	2.4	1.5	1.1
(25)	3.3	3.3	2.6	2.2	2.5	2.6	1.6	1.2
(30)	3.4	3.4	3.2	2.9	3.0	2.8	1.9	1.3
(35)	3.6	3.4	3.4	3.2	3.2	3.0	2.3	1.5
(40)			3.6	3.4	3.3	3.1	2.6	2.2
(45)			3.7	3.6	3.4	3.2	3.0	2.9
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^3) k_1 s^{-1}	**1.09**	**0.97**	**0.949**	**0.797**	**0.73**	**0.604**	**0.418**	**0.342**

Figures in parentheses denotes time in minutes

[Benzamide] Dependence

To know the effect of benzamide on Ag (I) catalysed autoxidation of S(IV) benzamide variation was carried out from $1x10^{-8}$ mol dm^{-3} to 5 x 10^{-4} mol dm^{-3} at two different Ag (I) that is $5x10^{-6}$ mol dm^{-3} and 1 x 10^{-5} mol dm^{-3} but fixed S(IV) = $2x10^{-3}$ mol dm^{-3} at pH = 4.95 and t = 30^o C. The results indicated that by increasing benzamide the rate becomes decelerates.



<u>Fig. 8.6</u> : Effect of catalyst at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, [Benzamide] = $7.0x10^{-7}$ mol dm^{-3}, t = 30^o C in acetate buffered medium. The value of intercept and slope are 6.7 x 10^{-4} s and 3.5 x 10^{1} mol dm^{-3} s respectively. Depending on the observed results the reaction follows the following rate law (8)

$$-d\,[S(IV)]/dt = (k_1+k_2[Ag(I)]\,[S(IV)] / 1 + B\,[Benzamide] \qquad (8)$$

$$\text{Where } k_{inh} = (k_1+k_2[Ag(I)] / 1 + B\,[Benzamide] = k_{cat} / 1 + B\,[Benzamide] \qquad (9)$$

$$1/k_{inh=} 1 + B\,[Benzamide] / k_{cat} \qquad (10)$$

$$1/\ k_{inh} = 1/\ k_{cat} + B\,[Benzamide] /\ k_{cat} \qquad (11)$$

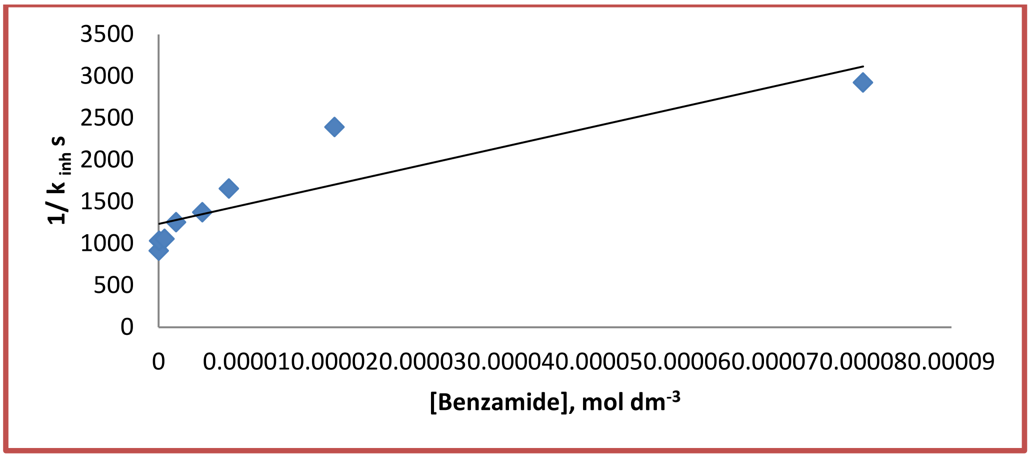


Fig. 8.6 : Effect of benzamide at [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C in acetate buffered medium. The plot of 1/ k_{inh} v/s [Benzamide] is linear with intercept 1.23 x 10^{3} s and slope 2.35 x 10^{7} mol dm^{-3} s from which the value of B = 1.91 x10^{4} mol dm^{-3}

Table - 8.30

The values of k_{inh} at different [Benzamide], [S(IV)] = 2x10^{-3} mol dm^{-3}, Ag (I) = 5x10^{-6} mol dm^{-3}, pH = 4.95, t = 30^{o} C CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH= 3x10^{-2} mol L^{-1}

[Benzamide] mol dm^{-3}	10^{3} k_{inh} s^{-1}	1/k_{inh} s
5.0x10^{-8}	0.929	1076
8.0x10^{-8}	0.898	1114
7.0x10^{-7}	0.842	1188
3.0x10^{-6}	0.650	1538
5.0x10^{-6}	0.607	1647
8.0x10^{-6}	0.430	2326
3.0x10^{-5}	0.3536	2828
5.0x10^{-5}	0.244	4098

Effect of Temperature

The values of k_{obs} were determined at three different temperatures in the range of 30^o C to 40^o C. The results are given in table 8.31 by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 17.05 KJ mol^{-1}

Table – 8.31

Effect of temperature k_{obs} air saturated suspensions at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, Ag (I) = 5 $x10^{-6}$ mol dm^{-3} [Benzamide] = 5.0 x 10^{-4} mol dm^{-3}, pH = 4.95

t^o C	$10^3\ k_{obs}\ s^{-1}$
30	0.842
35	0.924
40	1.01

Table - 8.32

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$ mol dm^{-3}, [Benzamide] = $7x10^{-7}$ mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	1	2	4	6	8	10
Time, (Min)	Volume of 5 $x10^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.6	1.2	2.2	3.1	3.5
(5)	0.7	0.9	1.6	3.1	4.8	5.2
(10)	0.9	1.4	2.5	3.9	5.7	6.8
(15)	1.2	1.9	3.3	4.7	7.2	7.7
(20)	1.4	2.4	4.5	5.5	8.8	9.1
(25)	1.6	2.8	5.5	6.7	10.5	10.9
(30)	1.6	3.2	6.6	7.9	11.7	13.9
(35)	1.7	3.4	6.8	9.7	13.8	15.7
(40)	1.8	3.6	7.0	11.3	14.7	18.9
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**0.902**	**0.924**	**0.900**	**0.902**	**0.916**	**0.906**

Figures in parentheses denotes time in minutes

Table- 8.33

Variation of [S(IV)] at Ag (I) =$1x10^{-5}$ mol dm^{-3}, [Benzamide] = $7x10^{-7}$ mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = $7x10^{-2}$ mol L^{-1}, CH_3COOH = $3x10^{-2}$ mol L^{-1}

10^3 [S(IV)] mol dm^{-3}	**1**	**2**	**4**	**6**	**8**	**10**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot					
(0)	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.6	1.0	2.5	3.5	3.5
(5)	0.8	0.9	1.7	3.2	4.7	5.5
(10)	0.9	1.5	2.4	4.9	6.1	7.1
(15)	1.1	2.1	3.3	6.2	7.8	8.9
(20)	1.3	2.5	4.5	7.8	8.9	10.5
(25)	1.5	2.9	5.6	9.5	10.2	13.5
(30)	1.7	3.3	6.7	10.2	13.9	16.5
(35)	1.8	3.6	7.2	10.6	14.8	18.5
∞	2.0	4.0	8.0	12.0	16.0	20.0
(10^3) k_1 s^{-1}	**1.00**	**1.01**	**1.02**	**1.01**	**1.06**	**1.04**

Figures in parentheses denotes time in minutes

Table- 8.34

Variation of Ag (I) at S(IV)] = 1 x10^{-3} mol dm^{-3}, [Benzamide] = 7x10^{-7}mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag (I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.4	0.8	0.8	0.6	0.6
(5)	0.6	1.0	1.0	0.9	0.9
(10)	0.9	1.3	1.3	1.3	1.3
(15)	1.0	1.5	1.5	1.5	1.5
(20)	1.2	1.6	1.6	1.6	1.7
(25)	1.4	1.7	1.7	1.8	1.9
(30)	1.6	1.8	1.9	1.9	1.9
(35)	1.7	1.9	1.9		
(40)	1.8	1.9			
∞	2.0	2.0	2.0	2.0	2.0
(10^3) k_1 s^{-1}	**0.881**	**1.19**	**1.35**	**1.44**	**1.70**

Figures in parentheses denotes time in minutes

Table- 8.35

Variation of Ag (I) at S(IV)] = 1x10^{-3} mol dm^{-3}, [Benzamide] = 7x10^{-7}mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7x10^{-2} mol L^{-1}, CH_3COOH = 3x10^{-2} mol L^{-1}

Ag(I) mol dm^{-3}	**5x10^{-6}**	**1x10^{-5}**	**1.5x10^{-5}**	**2x10^{-5}**	**2.5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot				
(0)	0.0	0.0	0.0	0.0	0.0
(2)	0.5	0.7	0.8	0.8	0.8
(5)	0.7	0.9	1.0	1.2	1.3
(10)	1.0	1.2	1.2	1.3	1.5
(15)	1.2	1.4	1.4	1.5	1.8
(20)	1.3	1.7	1.6	1.8	1.9
(25)	1.5	1.7	1.8	1.9	1.9
(30)	1.6	1.8	1.9	1.9	1.9
(35)	1.8	1.9			
∞	2.0	2.0	2.0	2.0	2.0
(10^{3}) k_1 s^{-1}	**0.937**	**1.28**	**1.46**	**1.67**	**1.84**

Figures in parentheses denotes time in minutes

Table- 8.36

Variation of benzamide at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) =5×10^{-6} mol dm^{-3}, pH = 4.95, t = 35^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH = 3×10^{-2} mol L^{-1}

[Benzamide] mol dm^{-3}	**5x10^{-8}**	**8x10^{-8}**	**7x10^{-7}**	**2x10^{-6}**	**5x10^{-6}**	**8x10^{-6}**	**2x10^{-5}**	**5x10^{-5}**
Time, (Min)	Volume of 5 x10^{-3} mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.8	0.8	0.6	0.7	0.7	0.6	0.6	0.4
(5)	1.2	1.1	0.9	1.1	1.0	1.1	0.8	0.6
(10)	1.5	1.5	1.5	1.3	1.4	1.5	1.0	0.8
(15)	1.9	1.9	1.9	1.4	1.8	2.1	1.2	1.0
(20)	2.4	2.6	2.4	1.6	2.1	2.5	1.4	1.2
(25)	2.9	3.3	2.7	2.1	2.5	2.7	1.5	1.3
(30)	3.3	3.3	3.1	2.6	2.9	2.9	1.9	1.6
(35)	3.6	3.4	3.4	3.2	3.2	3.0	2.4	1.8
(40)			3.5	3.5	3.3	3.1	2.6	2.3
(45)			3.7	3.5	3.4	3.1	2.9	2.5
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**0.985**	**0.949**	**0.908**	**0.76**	**0.702**	**0.574**	**0.417**	**0.319**

Figures in parentheses denotes time in minutes

Table- 8.37

Variation of benzamide at [S(IV)] = 2×10^{-3} mol dm^{-3}, Ag (I) =5×10^{-6} mol dm^{-3}, pH = 4.95, t = 40^{o} C, CH_3COONa = 7×10^{-2} mol L^{-1}, CH_3COOH = 3×10^{-2} mol L^{-1}

[Benzamide] mol dm^{-3}	**5×10^{-8}**	**8×10^{-8}**	**7×10^{-7}**	**2×10^{-6}**	**5×10^{-6}**	**8×10^{-6}**	**2×10^{-5}**	**8×10^{-5}**
Time, (Min)	Volume of 5 x10 $^{-3}$ mol dm^{-3} Hypo for 5 ml aliquot							
(0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(2)	0.9	0.8	0.8	0.8	0.7	0.6	0.7	0.8
(5)	1.2	1.2	1.1	1.2	1.0	1.1	0.8	1.3
(10)	1.6	1.5	1.5	1.3	1.4	1.5	1.1	1.7
(15)	1.9	1.9	1.9	1.6	1.8	2.1	1.3	2.0
(20)	2.4	2.7	2.5	1.8	2.1	2.5	1.5	2.3
(25)	3.5	3.4	2.8	2.2	2.5	2.7	1.6	2.4
(30)	3.6	3.4	3.5	3.0	3.0	2.9	2.3	2.4
(35)			3.5	3.6	3.4	3.0	2.9	2.4
∞	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
(10^{3}) k_1 s^{-1}	**1.21**	**1.08**	**0.989**	**0.848**	**0.787**	**0.666**	**0.481**	**0.417**

Figures in parentheses denotes time in minutes

DISCUSSION

In aqueous solutions SO_2 is present in four forms $SO_2.H_2O$, HSO_3^{-1}, SO_3^{-2}, $S_2O_3^{-2}$ In the experimental range of pH the following equilibrium operates.

$$HSO_3^{-1} \rightleftharpoons H^+ + SO_3^{-2} \qquad (12)$$

The equilibrium constant is $5.07x\ 10^{-7}$ In the experimental range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. During the course of reaction fraction order obtain is 0.23 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz, (2008)[19] Bigelow et al (1898)[4] studied the effect of alcohols on the reactions between sodium sulphite and O_2 and found that the alcohols inhibited the reaction rate. Alyea et al (1929)[1] studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Backstrom (1934)[2] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2. Grgic et al (1998)[10] studied the inhibition effect of acetate, oxlate, format on Fe - catalysed autoxidation of S(IV) at pH 2.8, 3.7,4.5 and found that oxlate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe^{+3} due to formation of complexion with oxlate. Bostjan et al (2006)[13] studied the effect of carboxylic acid on Mn (II) catalysed oxidation of S(IV) and found that monocarboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag (I) catalysed reaction is decelerated by the addition of benzamide in the present study. Gupta et al (2008)[14] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3 - 10^4 In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S (IV) by benzamide are found to be 4.78×10^4 mol dm^{-3} and 1.91×10^4 mol dm^{-3} respectively. These values are in the same range as reported by Gupta et al. This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick and Zhang (1996)[7]

$$HSO_3^{-1} \xrightleftharpoons{K_d} H^+ + SO_3^{-2} \quad K_d = 5.01 \times 10^{-7,\,18} \qquad (13)$$

$$Ag^+ + {}^-O_2CCH_3 \xrightleftharpoons{K_{oAc}} AgO_2CCH_3 \quad K_{oAc} = 2.29^{33} \qquad (14)$$

$$Ag^+ + SO_3^{-2} \xrightleftharpoons{K_1} AgOSO_2^- \quad K_1 = 2.51 \times 10^{5},^{29} \qquad (15)$$

$$Ag^+ + HSO_3^{-1} \xrightleftharpoons{K_2} AgHSO_3 \qquad (16)$$

$$AgOSO_2^- + O_2 \xrightleftharpoons{K_3} AgOSO_2^{-1}.O_2 \qquad (17)$$

$$AgHSO_3 + O_2 \xrightleftharpoons{K_4} AgHSO_3.O_2 \qquad (18)$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (19)$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} SO_4^{-\bullet} + SO_3^{-\bullet} + H_2O \qquad (20)$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + SO_3^{-\bullet} + O_2 \qquad (21)$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_4} SO_5^{-\bullet} \qquad (22)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_5} SO_3^{-\bullet} + SO_5^{-2} \qquad (23)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \qquad (24)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \qquad (25)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \qquad (26)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_9} \text{Non Chain product} \qquad (27)$$

$$SO_4^{-\bullet} + \text{Benzamide} \xrightarrow{k_{10}} \text{Non Chain product} \qquad (28)$$

By assuming long chain hypothesis and steady state approximation $d[SO_3^{-\bullet}]/dt$, $d[SO_4^{-\bullet}]/dt$, $d[SO_5^{-\bullet}]/dt$, to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 29)

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Benzamide}]\}\,[SO_4^{-1}] \qquad (29)$$

Since the reaction is completely stopped in the presence of [Benzamide] at 8×10^{-5} mol dm^{-3}, so the step (22) and (25) appear to be unimportant. The step

(24) is ignored because the reaction is completely seized in the presence of higher concentration of benzamide by omission and substitution from the above mechanism the following rate law can be obtain (30)

$$R_{cat} = k_1 [Ag(I)] [S(IV)] / \{k_9[x] + k_{10} [Benzamide]\} \quad (30)$$

Prasad et al. (2013)[31] and Gupta et al. (2008)[13] proposed a similar mechanism for the Co_2O_3 and CoO catalysed autoxidation of SO_2 inhibited by formic acid and ethanol respectively, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 1.91×10^4 mol dm^{-3} which is in the range of 10^3-10^4 and also coincide with the reported value of B of Co_2O_3 catalysed autoxidation of S(IV) by formic acid is 3.58×10^3 mol dm^{-3} So on the basis of calculated value of B we concluded that benzamide act as an free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

CONCLUSIONS

The following conclusions are deduced from the results of the benzamide inhibited Ag(I) catalysed autoxidation of S(IV) was that inhibit the oxidation with the fast influence. The value of Inhibition factor of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are in the range of 10^3 -10^4 which shows that free radical mechanism is operative.

REFERENCES

1. Alyea H.N., Backstrom H.L.J., (1929), The inhibitive action of alcohols on the autoxidation of sodium sulfite, *J Am Chem Soc*, **51**, 90–107.
2. Avery G.B., Brown J.L., Kiebeer (2009), Assessment of rainwater volatile organic carbon in southeastern North Carolina, USA, *Atmos Environ,* **43,** 2678–2681.
3. Backstrom H. L. J., (1934), The chain mechanism of the autoxidation of sodium sulfite solutions, *J. Phys. Chem.*(B), **25**, 122-138.
4. Bigelow S. L., (1988), Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.
5. Brandt C., Van Eldik R. (1995), Transition metal catalyzed oxidation of aqueous sulfur(IV) oxides. Atmospheric relevant process and mechanisms. Chem Rev 95:119–190.
6. Campos M.L.A., Nogueira R.F.P., Dametto P.R., Francisco J.G., Coelho CH, (2007), Dissolved organic carbon in rainwater, glassware decontamination and sample preservation and volatile organic carbon, *Atmos Environ*, **41**, 8924–8931.
7. Coichev N, van Eldik R, (1991), Kinetics and mechanism of the sulfite induced autoxidation of cobalt(II) in aqueous azide medium. *Inorg Chem,* **30**, 2375–2380.
8. Connick RE, Zhang YX (1996), Kinetics and mechanism of oxidation of HSO_3^- by O_2, the manganese(II) catalyzed reaction. *Inorg Chem*., **35**, 4613–4621.
9. Connick RE, Zhang YX, Lee S, Adamic R, Chieng P., (1995), Kinetics and mechanism of the oxidation of HSO_3- by O_2, the uncatalyzed reaction, *Inorg Chem.,* **34** , 4543–4553.
10. Grgic I, Hudnik V, Bizjak M, Levec J., (1991), Aqueous S(IV) oxidation-I. Catalytic effects of some metal ions, *Atmos Environ,* **25A**,1591–1597.

11. Gupta K.S. (2012), Aqueous phase atmospheric oxidation of sulfur dioxide by oxygen, role of trace atmospheric constituents-metals, volatile organic compounds and ammonia. *J Indian Chem Soc*, **89**, 713–724.
12. Gupta K.S., Manoj Mudgak PK, Sreedharan, (2008), Kinetic of iron(III) catalysed autoxidation of S(IV) in acetate buffered medium, *transition metal chem.*, **33**, 3111-316.
13. Gupta K.S., Mehta R.K., Sharma A.K., Mudgal P.K., Bansal S.P., (2008), Kinetics of uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 catalyzed autoxidation of sulfur(IV) in alkaline medium, *Transit Met Chem,* **33**, 809-817.
14. Hester R.E., Harrison R.M., Derwent R.G., (1995), Sources distributions and fates of VOCs in the atmosphere. In: Harrison RM, Hester RE (eds) Volatile organic compounds in atmosphere, vol 4, Royal Chemical Society, London, pp 1–16.
15. Huss A., Lim P.K., Eckert C.A., (1982), Oxidation of sulfur dioxide, the effects of chelating agents and phenolic antioxidants, *J Phys Chem,* **86**, 4233–4237.
16. Irena Wilkosz, Anna Mainka, (2008), Mn(II) catalysed and its inhibition by acetic acid in aq. Phase, *J of atm chem.*, **60,** 1-17.
17. Jain U., Sharma M., Rani A., Gupta K.S., (1995), Kinetics and mechanism of copper(II) catalyzed autoxidation of aqueous sulfur dioxide in acetate buffers. *Indian J Chem*, **34A**, 971–975.
18. L.G. Sillen and A.E. Martell, (1964), stability constants of metal ion complex special publication no 17, the chemical soc. Burlington house London.
19. Lee Y.J., Rochelle G.T., (1987), Oxidative degradation of organic acid conjugated with sulfite oxidation in flue gas desulfurization, products, kinetics and mechanism, *Environ Sci Technol*. **21**, 266–271.

20. Linn D.E. Jr, Dargan MJ, Miller D.E., (1990), Catalysis of the autoxidation of aqueous sulfur dioxide using [NiIII(cyclam)], evidence for a novel radical chain mechanism. *Inorg Chem*, **29,** 4356.
21. Lunak S, El-Wakil A, Veprek-Siska J., (1978), Autoxidation of sulfite catalyzed by 3d transition metals and inhibited by 2-propanol, mechanism of inhibited and induced reactions, *Collect Czechoslov Chem Commun*, **43**, 3306–3316.
22. Manabu G., Norimide N., Hiroshi O., (1999), Determination of volatile organic compounds in rainwater and the dominant factors of their concentrations. *Atomos Environ*, **34**, 211–218.
23. Manoj S.V., Mudgal P.K., Gupta K.S., (2008), Kinetics of iron(III) catalyzed autoxidation of sulfur(IV) in acetate buffered medium, *Transit Met Chem (Weinh)*, **33**, 311–316.
24. Manoj S.V., Singh R., Sharma M., Gupta K.S., (1999a), Kinetics and mechanism of heterogeneous cadmium sulfide and homogenous manganese(II) catalyzed oxidation of sulfur(IV) by dioxygen in acetate buffered medium. *Indian J Chem*, **39A**, 507–521.
25. Martin L.R., Hill M.W., Tai A.F., Good T.W., (1991), The iron catalyzed oxidation of sulfur(IV) in aqueous solution, different effects of organics at high and low pH, *J Geophys Res*, **D2**, 3085–3097.
26. Mudgal P.K., Sharma A.K., Mishra C.D., Bansal S.P., Gupta K.S., (2008), Kinetics of ammonia and ammonium ion inhibition of the atmospheric oxidation of aqueous sulfur dioxide by oxygen, *J Atmos Chem*, **61**, 31–55.
27. Okochi H., Kataniwa M., Sugimoto D., Igaw M., (2005), Enhanced dissolution of volatile organic compounds into urban dew water collected in Yokohama, Japan, *Atmos Environ*, **39**, 6027–6036.
28. Prasad D.S.N., Rani A., Gupta K.S. (1992), Surface-catalyzed autoxidation of sulfur(IV) in aqueous silica and copper(II) oxide suspensions, *Environ Sci Technol*, **26**, 1361–1368.
29. R. Van Eldik and G.M., (1980), *Harris Inorg Chem.*, **19**, 880.

30. Rodhe H., Dentener F., Schulz M., (2002), The global distribution of acidifying wet deposition, *Environ Sci Technol*, **36(20)**, 4382–4388.
31. Sameena Begam, Faiyaz Huusain, D.S.N. Prasad, (2013), Kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of S(IV) in alkaline medium, *Pelagia research library*,**4 (1)**, 122-131.
32. Sharma A.K., Singh A., Mehta R.K., Sharma S., Bansal S.P., Gupta K.S. (2011), Kinetics of copper(II)-catalyzed oxidation of S(IV) by atmospheric oxygen in ammonia buffered solutions. *Int J Chem Kinet*, **43**, 379–392.
33. V.F. Toropova I.A. Sirotina and V.B. Rotanova Uchenye Zapiski, (1955), Kazanskogo Uni. 115 no.3, 53.
34. Ziajka P., Pasiuk-Bronikowska W., (2003), Autoxidation of sulphur dioxidein the presence of alcohols under conditions related to tropospheric aqueous phase. *Atmos Environ*, **37**, 3913–3922.

BIBLIOGRAPHY

1. Altwicker E. R., (1980), In *Advances in Environmental Sciences and Engineering*, **Vol. 3.** J. R. Pfaffin and E. N. Zieglar(Eds.), Gordon and Breach Science Publishers, New York, pp 80-91.
2. Alyea H. N. and Backstrom H. L. J., 1929, The inhibitive action of alcohols on the autoxidation of sodium sulfite*, Journal of American Chemical Society,* 51, 90-107**.**
3. Anast J. M. and Margerum D. W., 1981, Trivalent copper catalysis of the autoxidation of sulfite, Kinetics and mechanism of the copper(III/II) tetraglycine reactions with sulfite, *Inorganic Chemistry*, **20**, 2319.
4. Ashmore P. G., (1963), *Catalysis and Inhibition of Chemical Reactions*. Butterworths, London.
5. Backstrom H. L. J., 1934, The chain mechanism of the autoxidation of sodium sulfite solutions, *J. Phys. Chem.*(B), **25**, 122-138.
6. Bhargava P. and Gupta K. S., 1993, Kinetics of oxidation of sulfur(IV) by peroxodisulfate, Relative reactivity of bisulfite and sulfite ions, *Indian Journal of Chemistry*, **32A**, 201-204.
7. Bhargava R., Prasad D. S. N., Rani A., Bhargava P., Jain U. and Gupta K. S., 1992, Kinetics of autoxidation of aqueous sulfur dioxide in suspensions of nickel(III) oxide, *Transition Metal Chemistry*, **17**, 238-241.
8. Bhargava R., Rani A. and Gupta, K. S., 1992, Surface-mediated oxidation of aqueous sulfur dioxide in ceramic powder suspensions, *Indian Journal of Chemistry*, **31A,** 683-687.
9. Bhargava R., Rani, A. and Gupta, K. S., 1993, Oxidation of aqueous sulfur dioxide in suspensions of magnesium dioxide, Removal of SO_2 from flue gases, *Indian Journal of Chemistry*, **32A,** 713-716.
10. Bigelow S. L., 1988, Catalytic effects in the oxidation of sodium sulfite by air oxygen, *Zeitschriftfuer Physikalische Chemie,* **26**, 493-532.

11. Brandt C. and Van Eldik, R., 1995, Transition metal catalyzed oxidation of aqueous sulfur(IV) oxides, Atmospheric Relevant Process and Mechanisms**,** *Chemical Reviews,* **95**, 119-190.
12. Buxton G.V., Salmon G.A., 2003, On the chemistry of inorganic free radicals in cloud water. Progress in Reaction Kinetics and Mechanism 28, 257–297.
13. Buxton G.V., Wang J., Salmon G.A., 2001, Rate constants for the reactions of NO_3, SO_4 – and Cl radicals with formate and acetate esters in aqueous solution, *Physical Chemistry Chemical Physics*, **3**, 2618–2621.
14. Calvert J. G. and Stockwell W. R., 1984, Mechanisms and rates of sulfur dioxides in atmosphere. In: *SO_2, NO and NO_2 Oxidation Mechanisms. Atmospheric Considerations,* J. G. Calvert (Ed.), Butterworths, Boston, pp1-62.
15. Chebbi A., Carlier P., 1996, Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review. *Atmospheric Environment, **30***, 4233–4249.
16. Clemitshaw K. C., 2006, Coupling between the trophospheric photochemistry of nitrous acid (HONO) and nitric acid (HNO_3), *Environmental Chemistry*, **3**, 31-34.
17. Clifton C. L. and Huie R. E., 1989, Rate constants for hydrogen abstraction reactions of the sulfate radical, SO_4^-, Alcohols, *International Journal of Chemical Kinetics,* **21,** 677-687.
18. Dogliotti L. and Hayon E., 1967, Flash photolysis of persulfate ions in aqueous solution, Study of sulfate and ozonide radical anions, *Journal of Physical Chemistry,* **71**, 2511-2516.
19. Exner M., Herrmann H., Zellner R., 1994, Rate constants for the reactions of the NO_3 radical with HCOOH/HCOO- and CH_3COOH/CH_3COO^- in

aqueous solution between 278 and 328 K, *Journal of Atmospheric Chemistry*, **18**, 359–378.

20. Fuzzi S., 1978, Study of iron(III) catalyzed sulfur dioxide oxidation in aqueous solution over a wide range of pH, *Atmospheric Environment,* **12,** 1439-1442.
21. Gilvert B. C., Stell J. K., Peet W. J. and Radford K. J., 1988, Generation and reaction of the chlorine atom in aqueous solution, *Journal of Chemical Society, Faradey Transactions,* **1,** 84, 3319-3330.
22. Grgic I., Dovzan A., Bercic, G., and Hudnik, V., 1998, The effect of atmospheric organic compounds on the Fe-catalyzed S(IV) autoxidation in aqueous solution, *J. Atmos. Chem.* **29**, 315–337.
23. Gupta K. S., 2002, Acid Rain Precursors, Sources Control and Damaging Effects, In *Proceedings Second SERC School on Mathematical Modelling of Atmospheric Pollution*, Sapna Book House, Bangalore, pp.7-12.
24. Gupta K. S., 2002, Global Climate Change: Green House Effect, In, *Proceedings Second SERC School on Mathematical Modelling of Atmospheric Pollution*, Sapna Book House, Bangalore, pp.13-24.
25. Gupta K. S., Jain U., Singh A., Mehta R. K., Manoj S. V., Prasad D. S. N., Sharma A., Parashar P., Bansal S. P., 2004, Kinetics and mechanism of the osmium(VIII)-catalysed autoxidation of aqueous sulfur dioxide in acidic and alkaline media. *Journal of Indian Chemical Society*, **81**, 1083-1092.
26. Gupta K. S., 2002, Air Pollution. In: Proceedings of Second SERC School on *'Mathematical Modelling of Atmospheric Pollution'* UGC-CAS in Fluid Mechanics, Sapna Book House, Banglore, pp 7-11.
27. Gupta K. S., Bhargava P., Manoj S. V. and Bhargava R., 2000, Kinetics and mechanism of silver(I) catalyzed oxidation of aqueous sulfur(IV) in acetate buffered medium. *Transition Metal Chemistry***,** **25**, 329-332.

28. Gupta K. S., Singh R., Saxena D., Manoj S. V. and M. Sharma., 1999, Role of manganese dioxide in the autoxidation of sulfur(IV) in oxic and anoxic suspensions, *Indian Journal of Chemistry*, **38A**, 1129-1138.
29. Gupta K.S., Bhargava P. and Manoj S.V., 1999, Kinetics of silver(I) catalysed oxidation of sulfur(IV) by peroxodisulfate, *Indian Journal of Chemistry,* **38A**, 692-697.
30. Gupta K.S., Bhargava P. and Manoj S.V., 2000, Kinetics of tetraamminecopper(II) catalysed oxidation of sulfur(IV) by peroxydisulphate in ammonia buffer, *Transition Metal Chemistry*, **25**, 274-278.
31. Gupta K.S., Bhargava P. and Manoj S.V. 2001, Kinetics of diamminesilver(I)-catalysed oxidation of sulfur(IV) by dioxygen in ammonia buffers, *Transition Metal Chemistry*, **26**, 71-75.
32. Gupta K.S., Mehta R.K., Sharma, A.K. Mudgal, P.K. Bansal S.P., 2008, Kinetics of the uninhibited and ethanol-inhibited CoO, Co_2O_3 and Ni_2O_3 Catalyzed autoxidation of Sulfur(IV) in alkaline medium, *Transition Metal Chemistry*, **33**, 809-817.
33. Hayon E., Treinin A. and Wilf J. 1972, Electronic spectra, photochemistry and Autoxidation mechanism of the sulfite-bisulfite pyrosulfite systems, The SO_2^-, SO_3^-, SO_4^- and SO_5^- radicals, *Journal of American Chemical Society*, **94**, 47-57.
34. Herrmann H., 2003, Kinetics of aqueous phase reactions relevant to atmospheric chemistry, *Chemical Reviews,***103,** 4691-4716.
35. Herrmann H., Exner M., Jacobi H.W., Raabe G., Reese A., Zellner R., 1995, Laboratory studies of atmospheric aqueous- phase free-radical chemistry: kinetic and spectroscopic studies of reactions of NO_3 and SO_4 radicals with aromatic compounds, *Faraday Discussions*, **100**, 129–153.

36. Hoffman M. R. and Jacob D. J., 1984, In *SO_2, NO and NO_2 Oxidation Mechanisms, Atmospheric Considerations*, Calvert, J.G.(Ed.), Butterworth, Boston, pp 101-172.

37. Hoffmann M. R. and Boyce S. D., 1983, In *Trace Atmospheric Constituents: Properties, Transformations and Fates*; S. E. Schwartz, (Ed.), John Wiley and Sons, New York, pp 147-189.

38. Hoffmann P., Karandashev V. K., Sinner T., and Ortner H. M., 1997, Chemical analysis of rain and snow samples from Chernogolovka/Russia by IC, TXRF and ICP-MS, *Fres. J. Anal. Chem.*, **357**, 1142–1148.

39. Huie R. E. and Neta P., 1984, Chemical behaviour of SO_3^- and SO_5^- radicals in aqueous solutions, *Journal of Physical Chemistry*,**23**, 5665-5669.

40. Huie R. E. and Peterson, N. C., 1983. In:*Trace Atmospheric Constituents; Properties, Transformations & Fates*; S. E. Schwartz, (Ed.), John Wiley and Sons, New York**,** pp 118-143.

41. Huie R. E. and Wayne Sieck L., 1999, In *S-Centered Radicals*; Alfassi, Z. B.(Ed.), John Wiley & Sons: New York, pp 63-99.

42. Huie R. E., 1995, In *Progress and Problems in Atmospheric Chemistry*, Barker, J.R (Ed.), World Scientific Publishing Co., Singapore, pp 374-419.

43. Huie R.E., Clifton C.L., 1996, Kinetics of the reaction of the sulfate radical with the oxalate anion. *International Journal of Chemical Kinetics*, **28**, 195–199.

44. Humphrey R. E., Ward M. H. and Hinze W., 1970, Spectrophotometric determination of sulfite with 4,4’-dithiopyridine and 5,5’dithiobis-(2-nitrobenzoic acid), *Anal. Chem*,. **42**, 698–702.

45. Huss A., Jr. Lim P. K. and Eckert C. A., 1978, On the ‘uncatalyzed’ oxidation of sulfur(IV) in aqueous solutions, *Journal of American Chemistry Soc*iety, **108**, 6253.

46. Huss Jr. A., Lim P. K. and Eckert C. A., 1982, Oxidation of aqueous sulfur dioxide. 1. Homogenous manganese(II) and iron (II) catalysis at low pH, *Journal of Physical Chemistry*, **86**, 4224-4228.

47. J. Ziajka, W. Pasiuk-Bronikowska, 2003, Autoxidation of sulphur dioxide in the presence of alcohols under conditions related to the tropospheric aqueous phase. *Atmos. Environ., **37***, 3913-3922.

48. Joos F. and Baltensperger U., 1991, A field study on chemistry, S(IV) oxidation rates and vertical transport during fog conditions, *Atmos. Environ.* **25A**, 217–230.

49. Kawamura K., Steiberg S., Ng L., Kaplan I.R., 2001, Wet deposition of low molecular weight mono- and di-carboxylic acids, aldehydes and inorganic species in Los Angeles. *Atmospheric Environment*, **35**, 3917-3926.

50. Kerminen V.-M., Ojanen C., Pakkanen T., Hillamo R., Aurela, M., Merilainen J., 2000, Low-molecular-weight dicarboxylic acids in an urban and rural atmosphere, *Journal of Aerosol Science*, **31**, 349–362.

51. Kotronarou A. and Sigg L., 1993, SO_2 oxidation in atmospheric water, Role of Fe(II) and effect of ligands, *Environ. Sci. Technol.* 27, 2725–2735.

52. Kraft J. and van Eldik R. 1989, Kinetics and mechanism of the iron(II1)-catalyzed autoxidation of sulfur(1V) oxides in aqueous solution, formation of transient iron(III)-sulfur(1V) complexes, *Inorganic Chemistry,* **28**, 2297-2305.

53. Kraft J. and van Eldik, R., 1989,The possible role of iron (III)-sulfur (IV) complexes in the catalysed autoxidation of sulfur (IV)-oxides, A mechanistic investigation, *Atmos. Environ.* **23**, 2709–2713.

54. Kuo D. T. F., Krik D. W. and Jia C. Q. 2006, The chemistry of aqueous S(IV)-Fe-O_2 system: state of the art, *Journal of Sulfur Chemistry*, **27**, 461-530.

55. Lee Y. J. and Rochelle, G. T. 1987, Oxidative degradation of organic acid conjugated with sulfite oxidation in flue gas desulfurization, products, kinetics and mechanism, *Environment Science and Technology,***21**, 266-271.
56. Leland J. K. and Bard, A. J., 1987, Photochemistry of colloidal semiconducting iron oxide polymorphs, *J. Phys. Chem.* **91**, 5076–5083.
57. Lente G. and Fabian I., 2002, Kinetics and mechanism of the oxidation of sulfur(IV) by iron(III) atmetal ion excess, *J. Chem. Soc., Dalton Trans.* 778–784.
58. Lunak S. and Veprek-Siska J., 1976, Photochemical autooxidation of sulfite catalyzed by iron(III) ions, *Coll. Czech. Chem. Commun.,* **41**, 3495–3503.
59. Manoj S. V., Mishra C. D., Sharma M., Rani A., Jain R., Bansal S. P. and Gupta K. S., 2000, Iron, manganese and copper concentrations in wet precipitations and kinetics of the oxidation of SO_2 in rain water at two urban sites, Jaipur and Kota, in western India, *Atmospheric Environment,* **34**, 4479-4486.
60. Manoj S. V., Singh R., Sharma M., Gupta K. S., 1999, Kinetics and mechanism of heterogeneous cadmium sulfide and homogenous manganese(II) catalyzed oxidation of sulfur(IV) by dioxygen in acetate buffered medium, *Indian Journal of Chemistry*, **39A**, 507-521.
61. Manoj S.V., Sharma M. and Gupta K.S., 1999, Role of cuprous oxide in autoxidation of aqueous sulfur dioxide and its atmospheric implications, *Atmospheric Environment*, **33,** 1503-1512.
62. Martin L. R., 1984, In *SO_2, NO and NO_2 Oxidation Mechanisms, Atmospheric Considerations*, Calvert, J. G. (Ed.), Butterworth, Boston**.** pp 63-100.
63. Martin L. R. and Good T. W., 1991, Catalysed oxidation of sulfur dioxide in solution, The iron–manganese synergism, *Atmos. Environ.,* **25A**, 2395-2399

64. Munger J. M., Jacob D. J., Waldman J. M. and Hoffmann M. R., 1983, Fogwater chemistry in an urban atmosphere, *J. Geophys. Res,.* **88**, 5109-5121.
65. Neususs C., Pelzing M., Plewka A., Herrmann H., 2000, A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles, methods and first results, *Journal of Geophysical Research*, **105**, 4513–4528.
66. Novic M., Grgic I., Poje M. and Hudnik V., 1996, Iron-catalyzed oxidation of S(IV) species by oxygen in aqueous solution, Influence of pH on the redox cycling of iron, *Atmos. Environ,.* **30**, 4191-4196.
67. Pasiuk-Bronikowska W., Bronikowski T., Ulejczyk M., 2003, Inhibition of the S(IV) autoxidation in the atmosphere by secondary terpenic compounds, *Journal of Atmospheric Chemistry*, **44**, 97-111.
68. Pasuik-Bronikowska W., Bronikowski T. and Ulejczyk M., 1997, Solubilization of organics un water coupled with sulfite Autoxidation, *Water Research*, **31**, 1767-1775.
69. Pasuik-Bronikowska W., Bronikowski T., Ulejczyk M., 1998, Chemical interactions of aqueous phase pollutants, Sulfur dioxide and sobrerol, in U. Schurath and R. Roselieb (Eds.), Proc. 2nd Workshop of the EUROTRAC-2 Subproject Chemical Mechanism Development, Forschungszentrum Aachen, Aachen, pp. A12/ 1-4.
70. Pasuik-Bronikowska W., Bronikowski T., Ulejczyk M., 1999, Oscillations in the rate of S(IV) autoxidation inhibited by sobrerol, in R. Vogt and G. Axelsdottir (Eds.), Proc. Joint Workshop, Ford Forschungszentrum Aachen, Aachen, pp. 195-198.
71. Pasuik-Bronikowska W., Bronikowski T., Ulejczyk M., 2000, Transformation of atmospheric constituents and pollutants induced by S(IV) Autoxidation,

Chemistry and kinetics. In: EUROTRAC-2 Annual Report, CMD Chemical Mechanism Development. ISS, Munich, pp 123-126.

72. Podkrajsek B., Bercic G., Tursic J., Grgic I., 2004, Aqueous oxidation of sulfur(IV) catalyzed by manganese(II), a generalized simple kinetic model, *Journal of Atmospheric Chemistry*, **47**, 287–303.
73. Podkrajsek B., Grgic I., Tursic J., Bercic G., 2006, Influence of atmospheric carboxylic acids on catalytic oxidation of sulfur(IV), *Journal of Atmospheric Chemistry*, **54**, 103–120.
74. Podkrajsek B., Grgic I. and Tursic J., 2002, Determination of sulfur oxides formed during the S(IV) oxidation in the presence of iron, *Chemosphere*, **49**, 271–277.
75. Prasad D. S. N., Mehta R. K. Parashar P., Madnawat P. V. S., Rani A., Singh U., Manoj S. V., Bansal S. P., Gupta K. S., 2003, Kinetics of surface-catalysed autoxidation of aqueous sulfur dioxide in cobalt(III) oxide suspensions, *Journal of Indian Chemical Society*, **80**, 391-394.
76. Prasad D. S. N., Rani A., Sharma M. and Gupta K. S., 1994, Rates of autoxidation of sulfur(IV) in aqueous suspensions of limestone powder, Implications for scrubber chemistry, *Indian Journal of Chemistry*, **1**, 87-92.
77. Prasad D. S. N., Rani A., Gupta K. S., 1992, Surface-Catalyzed oxidation of Sulfur(IV) in Aqueous silica and copper(II) oxide suspensions, *Environmental Science and Technology*, **26,** 1361-1368.
78. Prasad D. S. N., Rani A., Madnavat P. V. S., Bhargava R. and Gupta K. S., 1991, Kinetics of surface catalyzed oxidation of sulfur(IV) by dioxygen in aqueous suspensions of cobalt(II) oxide, *Journal of Molecular Catalysis*, **69**, 395-405.
79. Rani A., Prasad D. S. N., Bhargava R. and Gupta K. S., 1991, Dynamics of autoxidation of sulfur dioxide in aqueous suspensions of cadmium oxide, *Bulletin Chemical Society of Japan*, **63**, 1995-1961.

80. Rani A., Prasad D. S. N., Jain U. and Gupta K. S., 1991, Dynamics of multiphase glass powder catalysed autoxidation sulfur dioxide in bulk in aqueous phase, *Indian Journal of Chemistry*, **30A**, 756-764.

81. Rani A., Prasad D. S. N., Madnavat P. V. S., Gupta K. S., 1992, The role of free fall atmospheric dust in catalysing autoxidation of aqueous sulfur dioxide, *Atmospheric Environment,* **26A**, 667-673.

82. Rao X. and Collett Jr. J. L., 1995, Behavior of S(IV) and formaldehyde in a chemically heterogeneous cloud, *Environ. Sci. Technol.,* **29**, 1023–1031.

83. Rao X. and Collett Jr. J. L., 1998, The drop size-dependence of iron and manganese concentrations in clouds and fogs, Implications for sulfate production, *J. Atmos. Chem.,* **30**, 1023-1031.

84. Rudzinski K. A. and Pasuik-Bronokowska, 2001, Isoprene inhibition of S(IV) autoxidation initiated by peroxydisulfate, In *Transport and chemical Transformation in the Troposphere, Proc. EUROTRAC-2 Symp. 2000*, P. M. Midgley, M. J. Reuther and M. Williams (Eds.), Springer, Berlin, pp 1-4.

85. Sempere R., Kawamura, K. 2003, Trans-hemisphere contribution of C_2-C_{10} a, o-dicarboxylic acids and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochemical Cycles,* **17**, 1069.

86. Turpin B.J., Saxena P., Andrews E., 2000, Measuring and simulating particulate organics in the atmosphere problems and prospects, *Atmospheric Environment*, **34**, 2983-3013.

87. Wang H., Kawamura K., Yamazaki K., 2006, Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and Western Pacific Ocean, *Journal of Atmospheric Chemistry*, **53**, 43–61.

88. Wang H., Shooter D., 2004, Low molecular weight dicarboxylic acids in PM10 in a city with intensive solid fuel burning, *Chemosphere,* **56**, 725-733.

89. Warneck P. and Ziajka J., 1995, Reaction mechanism of the iron(III)-catalyzed autoxidation of bisulfite in aqueous solution, Steady state description for benzene as radical scavenger, *Ber. Bunsenges. Phys. Chem,.* **99**, 59-65.

90. Warneck P., Mirabel P., Salmon G.A., Van Eldik R., Vinckier C., Wannowius K.J., Zetzsch C., 1996, Transport and chemical transformation of pollutants in the troposphere, In Warneck, P. (Ed.), Heterogeneous and Liquid Phase Processes, vol. 2. Springer, Berlin, p p7-74

91. Wine P.H., Tang Y., Thorn R.P., Wells J.R., 1989, Kinetics of aqueous phase reactions of SO_4^- radical with potential importance in cloud chemistry, *Journal of Geophysical Research,* **94**, 1085-1094.

92. Wolf A., Deutsch F., Hoffmann P. and Ortner H. M., 2000, The influence of oxalate on Fe-catalyzed S(IV) oxidation by oxygen in aqueous solution, *Journal of Atmospheric Chemistry*, **37**, 125-135.

93. Yao X., Fang M., Chan C.K., 2002, Size distributions and formation of dicarboxylic acids in atmospheric particles. *Atmospheric Environment*, **36**, 2099–2107.

94. Ziajka J., Pasiuk-Bronikowska W., 2003, Autoxidation of sulphur dioxide in the presence of alcohols under conditions related to the tropospheric aqueous phase, *Atmospheric Environment*, **37**, 3913–3922.

95. Ziajka J., Pasiuk-Bronikowska W., 2005, Rate constants for atmospheric trace organics scavenging SO_4 in the Fe catalysed autoxidation of S(IV), *Atmospheric Environment*, **39**, 1431–1438.

96. Ziajka J., Beer F. and Warneck P., 1994, Iron-catalyzed oxidation of bisulfite aqueous solution, evidence for a free radical chain mechanism, *Atmospheric Environment*, **28(15)**, 2549-2552.

97. Zuo Y. and Chen H., 2003, Simultaneous determination of sulfite, sulfate, and hydroxyl methanesulfonate in atmospheric waters by ion-pair HPLC technique, *Talanta,* **59**, 875–881.

98. Zuo Y. and Hoigne J., 1992, Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes, *Environ. Sci. Technol.,* **26**, 1014–1022.

99. Zuo Y. and Hoigne J., 1993, Evidence for photochemical formation of H_2O_2 and oxidation of SO_2 in authentic fog water, *Science,* **260**, 71–73.

100. Zuo Y. and Hoigne J., 1994, Photochemical decomposition of oxalic, glyoxalic and pyruvic acid catalyzed by iron in atmospheric waters, *Atmos. Environ.,* **28**, 1231-1239.

101. Zuo Y. and Zhan J., 2005, Effects of oxalate on Fe-catalyzed photo oxidation of dissolved sulfur dioxide in atmospheric water, *Atmos. Environ,.* **39**, 27-37.

102. Zuo Y., 1994, Light-induced oxidation of bisulfite-aldehyde adducts in real fog water, *Naturwiss,* **81**, 505-507.

103. Zuo Y., 1995, Kinetics of photochemical/chemical cycling of iron coupled with organic substances in cloud and fog droplets, *Geochim Cosmochim Acta,* **59**, 3123-3130.

104. Zuo Y., 2003, Light-induced formation of hydroxyl radicals in fog waters determined by an authentic fog constituent, hydroxyl methane sulfonate, *Chemosphere,* **51**, 175-179.

ANNEXURES

ANNEXURE – 1

RESEARCH PAPERS PUBLISHED

- Paper entitled "*Utility and Application of FGD System (Flue Gas Desulphurization) in Chemical and Environmental Engineering*", has been published in **International Journal of Chemical Engineering and Applications** (IJCEA), 2012, Vol.3(2), 129-135.

- Paper entitled "*Study of different parameters for removal of Sulphur di oxide contained in flue gases to control air pollution at Rajasthan, India",* has been published in **2nd International Conference on Biology, Environment and Chemistry (ICBEC-2011)** at Dubai, UAE, 2011, 24, 9-13.

- Paper entitled "*Synthesis and Process for removal of Sulphur di oxide contained in flue gases in thermal plants",* has been published in **Rasayan Journal of Chemistry**, (RJC), 2010, Vol 03(2), 328 – 334.

- Paper entitled "*Kinetics and mechanism of uncatalysed and Ag (I) catalysed autoxidation of S(IV) and its inhibition by isoamyl alcohol in acidic aqueous solutions",* has been published in **International Journal of Modern Sciences and Engineering Technology (IJMSET)**,2015, Vol 2(12),31-40.

- Paper entitled "*Formic Acid inhibited Ag (I) Catalysed Autoxidation of S(IV) in Acidic Medium*", has been published in **Journal of Chemistry and Chemical Sciences**, 2015,Vol.5(12), 760-771

- Paper entitled "*Ag (I) catalysed autoxidation of S (IV) and its inhibition by isopropyl alcohol in acidic medium"***,** has been published in **Chemical Sciences Review and Letters,** 2016,*Vol.5(17)), 14-23*

ANNEXURE-2

PUBLICATIONS IN BOOKS

- *Applications of FGD Process for removal of Sulphur di Oxide*, “ISBN 978-3-8465-9329-5”, by LAP LAMBERT Academic Publishing is a trademark of AV Academic GmbH & Co. KG Heinrich-Bocking-Str. 6-8,66121, Saarbrucken, 2012, Germany. **www.lap-publishing.com**
- *Recovery and Reuse of SO_2 from Thermal Power Plant Emission*, Air Pollution - Monitoring, Modelling, Health and Control, Dr. Mukesh Khare (Ed.), ISBN: 978-953-51-0381-3, In Tech, DOI: 10.5772/32390. OPEN ACCESS PUBLISHER, University campus STePRiSlavkaKrautzeka 83/A, 51000 Rijeka Croatia EUROPE, **www.intechweb.org**

ANNEXURE-3

AWARDS AND DISTINCTIONS

- Awarded **Prof. V. S. Tripathi Young Scientist Award** by ICS KOLKATA, in 47th Annual convention of Chemists -2010 & International conference on Recent Advances in Chemical Sciences at Pt. R.S. University, Raipur (Chhattisgarh).
- Awarded **SRF by CSIR** in 2012.
- Awarded **International travel grant by CSIR**, New Delhi to attend 2nd (ICBEC-2011) at Dubai, UAE in 2011.
- **Best Performer Award** has been given by BARC-BRNS-AEACI-DAE in SAC-7 (7th School on analytical chemistry at Heavy Water Plant Manuguru A.P. in 2013.

ANNEXURE-4

PARTICIPATION IN SEMINARS/ SYMPOSIA/ CONFERENCES

1. Research Paper presented in *"National Conference on Environment health hazards"* on 17-18 December 2009 at **J.D.B. P.G. Govt. College for Women Kota**, Rajasthan, India.
2. Research paper presented in *"National Conference on Recent trends in chemical Science"* on 1-2 December 2009 at Department of Chemistry **P.G. Lohiya College Churu**, Rajasthan, India.
3. Research paper presented in three days *"National Seminar on Analytical Electro Chemistry"* on 8-10 February 2010 at Department of Chemistry **J.N.V. University Jodhpur**, Rajasthan, India.
4. Research paper presented in two days *"National Seminar on Conservation of Lakes and Water Resources Strategies"* on 19-20 Feb -2010 at **College of Technology and Engineering Maharana Pratap University of Agriculture and Technology Udaipur**, Rajasthan, India..
5. Research paper presented in three days "*National Seminar on Emerging views in Advanced Chemistry"* on 17-19 December 2010 at Department of Chemistry **M. L. V. Govt. College, Bhilwara**, Rajasthan, India.
6. Research paper presented in three days *"2nd International Conference on Biology, Environment and Chemistry (ICBEC-2011)"* on 28-30 December 2011 at **Dubai**, UAE.
7. Research paper presented in two days *"National Conference on Technological advancements in Chemical and Environmental Engineering (TACEE-2012)"* on 23-24 March 2012 at **BITS Pilani**, Rajasthan, India.
8. Research paper presented in five days *"47th Annual Convention of Chemists and Inter National Conference on Recent Advances in Chemical Sciences"* on 23-27 December at **Pt. Ravi Shanker Shukla University Raipur**, Chhattisgarh, India
9. Research Paper presented in two days *"National Seminar on Chemistry of primates : Green Chemistry*" on 29-30 November 2012 at Department of Chemistry, **Dayanand College Ajmer**, Rajasthan, India.

10. Research Paper presented in two days *"International workshop on climate change impacts and societal adaptations"* on 7-8 November 2013 at **Central University of Rajasthan**, Rajasthan, India.
11. Research Paper presented in *"Center of excellence annual research seminar"* on 20-21 January 2014 at **S.D. Govt. College Beawar**, Rajasthan, India.
12. Participated in Eight days workshop on *Seventh BRNS(Board of Research in Nuclear Science) and AEACI (Association of Environmental Analytical Chemistry of India), school on Analytical chemistry"* on 18-25 November 2013 at **Heavy Water Plant Manuguru**, Andhra Pradesh, India.
13. Two Posters presented in Five days "*102nd Indian Science Congress"* on 3-7 January 2015 at **University of Mumbai**, **Mumbai**, Maharashtra India.
14. Participated in One day *"National Seminar on Innovative teaching methodology for C 13 NMR Spectroscopy"* on 25 March 2015 at Pure and Applied Chemistry Department **M.D.S.U. Ajmer**, Rajasthan, India.
15. Two Research Papers Presented in Four days "*BRNS-AEACI symposium on Current trends in Analytical chemistry"* on 26-29 May 2015 at **Bhabha Atomic Research Center, Mumbai**, Maharashtra, India.
16. Participated in One day *"National Seminar on Mass Spectroscopy"* on 17 October 2015 at Pure and Applied Chemistry Department **M.D.S.U. Ajmer**, Rajasthan, India.
17. Research paper presented in three days *"52th Annual Convention of Chemists and Inter National Conference on Recent Advances in Chemical Sciences"* on 28-30 December 2015 at **JECRC University Jaipur**, Rajasthan, India.
18. Research Paper presented in two days *"National conference on Green Chemistry and sustainable technologies for society"* on 11-12 January 2016 at Department of Chemistry **Govt. Engineering College for Women Ajmer**, Rajasthan, India.

ANNEXURE-5

MEMBERSHIP OF PROFESSIONAL BODIES

- Life Member of (APCBEE) Asia-Pacific Chemical, Biological & Environmental Engineering Society - Hong Kong. (L- 200417).
- Life member of (ISCA) Indian Science Congress Association, Kolkata. (L- 25652).
- Life member of (AEACI) Association of Environmental Analytical Chemistry of India, Bhabha atomic research center Mumbai. (L-360).

SUMMARY

The thesis consists of eight distinct chapters:

Chapter-I: Introduction and literature reviewed on the subject

This chapter comprises an introductory idea about the studied area, SO_2emission and their sources in the environment and catalysis by different metal ions, metal oxides(Transition and Non-transition),anthropogenic material e.g. fly ash, automobile exhaust dust, metal sulphides, S.P.M. (suspended particulate matter) – free fall atmospheric dust etc. and inhibition by organic compounds i.e. (carboxylic acid, alcohol, amine, amide etc.) and a report of the literature reviewed on the subject along with the objectives and importance of the study. This chapter includes 111 references.

Chapter-II: Methods and methodology

Since our aim was to studying the role of organic compounds in atmospheric autoxidation of S (IV) in aqueous phase which is the major factor responsible for acidification of atmospheric system and acid rain. For this chemical kinetics studies has been selected. This chapter includes the source of chemicals, catalyst, the standardization method and procedure adopted for following reaction kinetics have been desired. The experimental procedure was exactly the same as described earlier by Brodzinsky et al (1980), Mudgal et al (2008), Gupta et al (2008) and is briefly given here. The all chemicals were used as analytical reagent (AR) grade and solutions were prepared in double distilled water. The reaction were conducted in 0.15 L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature $30\pm1\ ^0$C. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. The selection of suitable stirring speed is necessary to save the reaction from becoming oxygen mass transfer controlled. For this reason, the rate of reaction were studied at different stirring speeds measured with the help of a tachometer (Mudgal et al , 2008). This led us to select a stirring speed of 1600 ± 10 rpm for stirring the reaction mixture continuously and magnetically to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in buffer medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10 cm^3 buffer made from sodium acetate (0.07 mol L^{-1}) and acetic acid (0.03 mol L^{-1}) for acidic medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically. (Brodzinsky et al (1980), Mudgal et al (2008), Prasad et al (1992)and Gupta et al (2008). For this purpose 5.0 ml aliquot samples were withdrawn periodically and added to a titration flask containing known quantity of iodine. The unreacted iodine was titrated with standard sodium thio sulphate solution using starch as an indicator. The chapter includes the figure 2.1 indicating schematic diagram of the experimental set up for the kinetic study of S (IV) – O_2 oxidation reaction. This chapter includes 6 references

Chapter-III: Kinetics of formic acid inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic medium.

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. The role of formic acid as inhibitor of Ag (I) catalysed autoxidation of S (IV) in acidic buffer medium has been identified. Based on the observed results a free radical mechanism has been proposed and following rate law has been given.

$$-d\,[S(IV)/dt \;=\; (k_1+k_2[Ag])\,[S(IV)]/\,1 + \;B\,[\text{Formic acid}]$$

Experiment were carried out at $30 \le t°C \le 45, 4.02 \le pH \le 5.25$, 1×10^{-3} mol/$dm^3 \le$[S(IV)$\le 10\times10^{-3}$ mol/dm^3, 5×10^{-6}mol/$dm^3 \le$[Ag(I)]$\le 2.5\times10^{-5}$ mol/dm^3, 5×10^{-6}mol/$dm^3 \le$[formic acid]$\le 8\times10^{-4}$ mol/dm^3, Based on the experimental results, rate constants and order of the reactions were determined. Depending on the reaction conditions, the observed results for the Ag (I) catalysed S(IV) oxidation reaction in presence of formic acid has been tabulated and graphs have been plotted. The reaction order in S(IV) was first order for both reactions. The effect of Ag (I) ion and inhibitor concentrations as well as initial pH of the solution on S (IV) oxidation rate was discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but independent on pH change during reaction. The effect of temperature of solution on S (IV) oxidation catalysed by Ag(I) in presence of formic acid was discussed. The values of k_{obs} were determined at three different temperatures in the range of 30^oC to 40^oC By plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation for the reaction which is 79.3 KJ mol^{-1}In contrast our results conclusively showed that formic acid studied above act as an inhibitor not catalyst for S (IV) autoxidation. The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are 3.33×10^4mol $dm^{-3}$and 2.53×10^3 mol dm^{-3} which is in the range of 10^3-10^4as reported by Gupta et al (2008) and Prasad et al (2013).This chapter includes 28 references

Chapter-IV: Kinetics of isopropyl alcohol inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic medium

The kinetics of atmospheric autoxidation of S (IV) by Ag(I) in the pH range 4.02-5.25 has been studied. The role of isopropyl alcohol as an inhibitor of Ag(I) catalysed autoxidation of S (IV) in acidic buffer medium has been identified. Based on the observed results a free radical mechanism has been proposed and following rate law has been given.

$$-d\,[S(IV)/dt \quad = \quad (k_1+k_2[Ag])\,[S(IV)]/\,1 + \;B\,[\text{Isopropyl alcohol}]$$

Experiments were carried out at $30 \le t°C \le 45$, $4.02 \le pH \le 5.25$, 1×10^{-3} mol/$dm^3 \le$ [S(IV)$\le 10\times10^{-3}$ mol/dm^3, 5×10^{-6}mol/$dm^3 \le$[Ag(I)]$\le 2.5\times10^{-5}$ mol/dm^3, 5×10^{-7}mol/$dm^3 \le$[iso propyl alcohol]$\le 8\times10^{-4}$mol/dm^3.Based on the experimental results, rate constants and order of the reactions were determined. Depending on the reaction conditions, the observed results for the Ag (I) catalysed S(IV) oxidation reaction in presence of isopropyl alcohol as inhibitor have been tabulated and graphs have been plotted. The reaction order in S(IV) was first order for both reactions. The effect of Ag (I) ion and inhibitor concentration as well as initial pH of the solution on S (IV) oxidation rate was discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but it is independent on pH change during the reaction. The effect of temperature of solution on S (IV) oxidation catalysed by Ag(I) in presence of isopropyl alcohol was discussed. The values of k_{obs} were determined at three different temperatures in the range of 30^oC to 40^oC by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation for the reaction which is 71.83 KJ mol^{-1}In contrast our results conclusively showed that isopropyl alcohol studied above act as an inhibitor not catalyst for S (IV) autoxidation. The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are 4.92×10^4mol $dm^{-3}$and 2.03×10^3mol dm^{-3} which is in the range of 10^3 -10^4 as reported by Gupta et al (2008) and Prasad et al (2013). This chapter includes 31 references

Chapter-V: Kinetics of isoamyl alcohol inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic medium.

The kinetics of atmospheric autoxidation of S (IV) by Ag(I) in the pH range 4.02-5.25 has been studied. The role of isoamyl alcohol as an inhibitor of Ag(I) catalysed autoxidation of S (IV) in acidic buffer medium has been identified. Based on the observed results a free radical mechanism has been proposed and following rate law has been given.

$$-d\,[S(IV)/dt \;=\; (k_1+k_2[Ag])\,[S(IV)]/\;1 + \;B\,[\text{ Isoamyl alcohol}]$$

Experiments were carried out at $30 \le t°C \le 45$, $4.02 \le pH \le 5.25$, 1×10^{-3} mol/$dm^3 \le$ [S(IV)$\le 10\times10^{-3}$ mol/dm^3, 5×10^{-6}mol/$dm^3 \le$[Ag(I)]$\le 2.5\times10^{-5}$ mol/dm^3, 5×10^{-6}mol/$dm^3 \le$[isoamyl alcohol]$\le 3\times10^{-4}$mol/dm^3. Based on the experimental results, rate constants and order of the reactions were determined. Depending on the reaction conditions, the observed results for the Ag (I) catalysed S(IV) oxidation reaction in presence of isoamyl alcohol have been tabulated and graphs have been plotted. The reaction order in S(IV) was first order for both reactions. The effect of Ag (I) ion and inhibitor concentration as well as initial pH of the solution on S (IV) oxidation rate was discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but it is independent on pH change during the reaction. The effect of temperature of solution on S (IV) oxidation catalysed by Ag (I) in presence of isoamyl alcohol was discussed. The values of k_{obs} were determined at three different temperatures in the range of 30^oC to 40^oC by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation for the reaction which is 45.16 KJ mol^{-1}.In contrast our results conclusively showed that isoamyl alcohol act as an inhibitor not catalyst for S (IV) autoxidation. The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are 5.04 x 10^4mol $dm^{-3}$and 1.24 x 10 ^{4}mol dm^{-3}, which is in the range of 10^3 -10^4 as reported by Gupta et al (2008) and Prasad et al (2013). This chapter includes 30 references

Chapter-VI: Kinetics of sodium benzoate inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic medium.

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. The role of sodium benzoate as inhibitor of Ag (I) catalysed autoxidation of S (IV) in acidic buffer medium has been identified. Based on the observed results a free radical mechanism has been proposed and following rate law has been given.

$$-d\,[S(IV)/dt \;=\; (k_1+k_2[Ag])\,[S(IV)]/\,1 + \;B\,[\text{Sodium benzoate}]$$

Experiments were carried out at $30 \le t°C \le 45$, $4.02 \le pH \le 5.25$, 1×10^{-3} $mol/dm^3 \le$ $[S(IV) \le 10\times10^{-3}$ mol/dm^3, $5\times10^{-6} mol/dm^3 \le [Ag(I)] \le 2.5\times10^{-5}$ mol/dm^3, $8\times10^{-8} mol/dm^3 \le [$ Sodium benzoate$] \le 2\times10^{-4} mol/dm^3$. Based on the experimental results, rate constants and order of the reactions were determined. Depending on the reaction conditions, the observed results for the Ag (I) catalysed S(IV) oxidation reaction in presence of sodium benzoate have been tabulated and graphs have been plotted. The reaction order in S(IV) was first order for both reactions. The effect of Ag (I) ion and inhibitor concentration as well as initial pH of the solution on S (IV) oxidation rate was discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but it is independent on pH change during the reaction. The effect of temperature of solution on S (IV) oxidation catalysed by Ag (I) in presence of sodium benzoate was discussed. The values of k_{obs} were determined at three different temperatures in the range of 30^oC to 40^oC by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation for the reaction which is 24.11 KJ mol^{-1}.In contrast our results conclusively showed that sodium benzoate act as an inhibitor not catalyst for S (IV) autoxidation. The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are 3.68×10^4 mol $dm^{-3}$and 1.48×10^4 mol dm^{-3} which is in the range of 10^3 -10^4 as reported by Gupta et al (2008) and Prasad et al (2013). This chapter includes 24 references.

Chapter-VII: Kinetics of aniline inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic medium.

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. The role of aniline as inhibitor of Ag(I) catalysed autoxidation of S (IV) in acidic medium has been identified. Based on the observed results a free radical mechanism has been proposed and following rate law has been given.

$$-d\,[S(IV)/dt \;=\; (k_1+k_2[Ag])\,[S(IV)]/\,1 +\; B\,[Aniline]$$

Experiments were carried out at $30 \le t°C \le 45$, $4.02 \le pH \le 5.25$, 1×10^{-3} $mol/dm^3 \le [S(IV) \le 10\times10^{-3} mol/dm^3$,$5\times10^{-6} mol/dm^3 \le [Ag(I)] \le 2.5\times10^{-5} mol/dm^3$,$5\times 10^{-7} mol/dm^3 \le [Aniline] \le 8\times10^{-3} mol/dm^3$, based on the experimental results, rate constants and order of the reactions were determined. Depending on the reaction conditions, the observed results for the Ag (I) catalysed S(IV) oxidation reaction in presence of aniline has been tabulated and graphs have been plotted. The reaction order in S(IV) was first order for both reactions. The effect of Ag (I) ion and inhibitor concentration as well as initial pH of the solution on S (IV) oxidation rate was discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but it is independent on pH change during the reaction. The effect of temperature of solution on S (IV) oxidation catalysed by Ag(I) in presence of aniline was discussed. The values of k_{obs} were determined at three different temperatures in the range of 30^oC to 40^oC by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation for the reaction which is 26.43 KJ mol^{-1}. In contrast our results conclusively showed that aniline act as an inhibitor not catalyst for S (IV) autoxidation. The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are $1.86 \times 10^3 mol\ dm^{-3}$ and $3.68 \times 10^3 mol\ dm^{-3}$, which is in the range of 10^3 -10^4 as reported by Gupta et al (2008) and Prasad et al (2013).This chapter includes 42 references.

Chapter-VIII: Kinetics of benzamide inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic medium.

The kinetics of atmospheric autoxidation of S (IV) by Ag (I) in the pH range 4.02-5.25 has been studied. The role of benzamide as inhibitor in Ag (I) catalysed autoxidation of S (IV) in acidic buffer medium has been identified. Based on the observed results a free radical mechanism has been proposed and following rate law has been given.

$$-d [S(IV)/dt = (k_1+k_2[Ag]) [S(IV)]/ 1 + B [Benzamide]$$

Experiments were carried out at $30 \leq t°C \leq 45$, $4.02 \leq pH \leq 5.25$, $1\times10^{-3} mol/dm^3 \leq [S(IV) \leq 10\times10^{-3} mol/dm^3$, $5\times10^{-6} mol/dm^3 \leq [Ag(I)] \leq 2.5\times 10^{-5} mol/dm^3$, $1\times10^{-8} mol/dm^3 \leq [Benzamide] \leq 5\times10^{-5} mol/dm^3$, based on the experimental results, rate constants and order of the reactions were determined. Depending on the reaction conditions, the observed results for the Ag(I) catalysed S(IV) oxidation reaction in presence of benzamide have been tabulated and graphs have been plotted. The reaction order in S(IV) was first order for both reactions. The effect of Ag (I) ion and inhibitor concentration as well as initial pH of the solution on S (IV) oxidation rate was discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but it is independent on pH change during the reaction. The effect of temperature of solution on S (IV) oxidation catalysed by Ag (I) in presence of benzamide was discussed. The values of k_{obs} were determined at three different temperatures in the range of 30^oC to 40^oC by plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation for the reaction which is 17.05 KJ mol^{-1}In contrast our results conclusively showed that benzamide act as an inhibitor not catalyst for S (IV) autoxidation. The value of inhibition factor (B)of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the present study are $4.78 \times 10^3 moldm^3$and 1.91×10^4 mol dm^{-3} which is in the range of 10^3 -10^4as reported by Gupta et al (2008) and Prasad et al (2013). This chapter includes 34 references.

Inhibiting effect of formic acid, sodium benzoate, benzamide, aniline, isopropyl alcohol, isoamyl alcohol on Ag (I) catalysed autoxidation of S (IV) in acidic medium are as follows:

Name of Inhibitor	**Inhibition parameter (B) mol dm^{-3}**
Formic acid	3.33×10^4
Sodium benzoate	3.68×10^4
Benzamide	4.78×10^4
Aniline	1.86×10^3
Isopropyl alcohol	4.92×10^3
Isoamyl alcohol	5.07×10^4

The inhibition power of these inhibitors are in the order of aniline< isopropyl alcohol<formic acid< sodium benzoate< benzamide<isoamyl alcohol. The inhibition parameter lies in the range of 10^3 - 10^4as reported by earlier workof Gupta et al, Sameena et al, Prasad et al, these reactions follows free radical mechanism. These organic substances are potential inhibitors in the autoxidation of S (IV) in aqueous phase. Out of the six inhibitors undertaken for study in the present work, isoamyl alcohol shows higher inhibiting capacity as compared to other five inhibitors.

A systematic and alphabetized bibliography and annexures are given at the end of the thesis.

*****