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RESEARCH ARTICLE

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# The effect of atmospheric aromatic amides on the Ag (I) catalyzed S(IV) autoxidation in aqueous solution

**Abstract:**
The kinetics of atmospheric autoxidation of S (IV) by Ag(I) in the pH range 4.02-5.25 has been studied. The aqueous phase autoxidation of S (IV) is the major factor responsible for acidification of atmospheric aqueous system. The role of benzamide act as an inhibitor of Ag(I) catalysed autoxidation of S (IV) in acidic medium has been identified, and based on the observed results following rate law given and a free radical mechanismhas been proposed.

$$d[S(lV)]/dt \quad = \quad (k_1 + k_2[Ag(I)])\,[S(lV)]/1 + B\,[Benzamide]$$

Experiments were carried out at $30 \leq T°C \leq 40$, $4.02 \leq pH \leq 5.25$, $1\times10^{-3} mol/cm^3 \leq [S(IV)] \leq 10\times10^{-3} mol/cm^3$, $5\times10^{-6} mol/cm^3 \leq [Ag(I)] \leq 2.5\times10^{-5} mol/cm^3$, $1\times10^{-8} mol/cm^3 \leq [Benzamide] \leq 5\times10^{-3} mol/cm^3$. Based on the experimental results, rate constants and orders of the reactions were determined.The reaction order in S(IV) were first order for both reactions in the presence and absence of benzamide. The effect of Ag(I) ion and benzamide concentrations as well as an initial pH of the solution on the S(IV) oxidation rate were discussed. It was found that the rate of the S(IV) oxidation depends on the initial pH of the solution but it is independent of the pH change during the reaction. Addition of benzamide leads to the introduction of an induction period and decrease in reaction rate, most likely due to $SO_4^{-1}$ radicals. The value of apparent energy and inhibition constant B were calculated in the presence of benzamide found as17.05 KJ $mol^{-1}$ and 4.78 x $10^4 mol\ dm^{-3}$ respectively.

**Keywords:**Kinetics; Autoxidation; S(IV); Ag(I); Catalysis; Inhibition ;Benzamide

## 1. Introduction:

Transition metal ions and their complexes present in atmospheric liquid water are considered tobe potential catalysts in the autoxidation of S(IV) oxides (Brandt and van Eldik, 1995[1]Grgic1998[2]. The catalytic activity of metal ions depends strongly on the conditions in thereaction system, particularly on the oxidation state of the metal ion, on the concentration range ofthe active species and on the pH of the reaction solution. In spite of many investigations on metalion catalysis, there are still discrepancies, particularly for Ag (I) catalysis at pH above 4. Ag (I) is potentially capable of replacing iron as catalyst in S(IV) autoxidation.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),[3]Clemitshaw (2006),[4] Calvert and Stockwell,(1984),[5] Huie and Peterson, (1983),[6] Hoffmann and Boyce (1983),[7] Hoffmann and Jacob(1984),[8] Hermann,(2003),[9] Huie and Wayne Seick, (1999),[10] Gupta (2011),[11] Rani et al. , (1995),[12] Manoj et al. , (2000)[13] Prasad et al., (1992),[14] Martin, (1991).[15]Alternatively, many organic compounds (e.g., oxalate, acetate formate, glycolate) are very common constituents of aerosols and can be transferred into the liquid phase. Grgic2007[16] These compounds can alter the usual aqueous phase chemistry and thus should be considered in atmospheric calculations.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.

## 2. Experimental:

The experimental procedure was exactly the same as described earlier.[17] 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 $30\pm1^0$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 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±1 %. All calculations were performed in MS Excel.

## 3. 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)

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

## 4. Results:

### 4.1 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 °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 Figure 1 from the figure 1 it is observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by Benzamide.

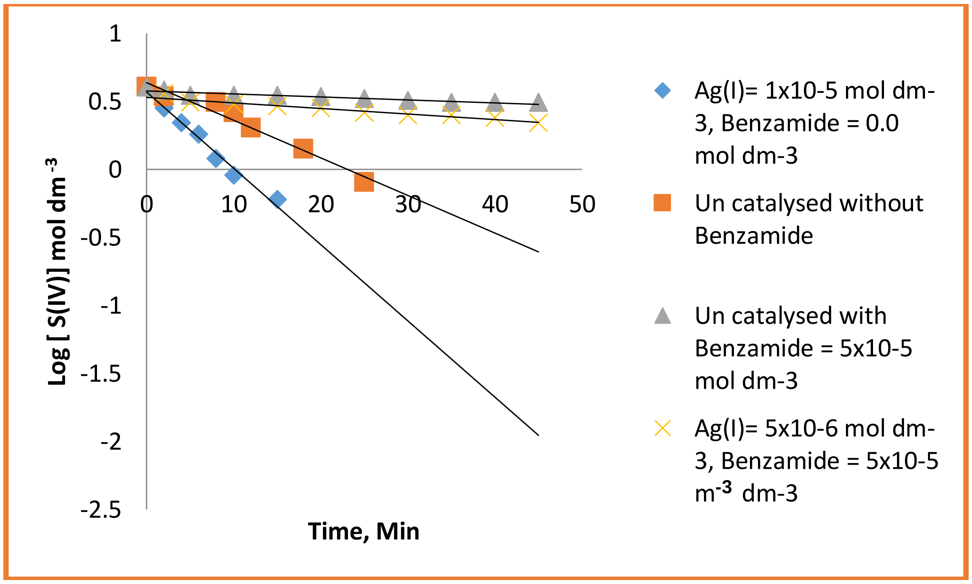

**Figure 1The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] =2 x $10^{-3}$mol $dm^{-3}$ at pH = 4.95, t = 30° C.**

( ◇) Ag (I) = 1x $10^{-5}$mol $dm^{-3}$, [Benzamide] = 0.0 mol $dm^{-3}$
( □) Uncatalysed without Benzamide
( △) Uncatalysed with [Benzamide] = 5x$10^{-5}$ mol $dm^{-3}$
( x ) Ag (I) = 5x $10^{-6}$mol $dm^{-3}$, [Benzamide] = 5x $10^{-5}$mol $dm^{-3}$

### 4.2 Uncatalysed Reaction

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

### 4.3 Dependence of S (IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it is in the range 1x$10^{-3}$mol $dm^{-3}$ to 4x$10^{-3}$mol $dm^{-3}$ at pH = 4.95, t = 30 °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 values of first order rate constant k1 are given in **Table 1**. The dependence of reaction rate on [S(IV)] follows the rate law (2)

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

**Table 1** The values of $k_1$ for uncatalysed reaction at different [S(IV)] , 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 |

### 4.4 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 2** 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)

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

The values of $k_{inh}$in the presence of Benzamide decreased with increasing [Benzamide] are given in **Table 2** 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. The values of intercept (1/ $k_1$) and slope (B/ $k_1$) were found to be 1.68 x $10^3$ s and 8.07 x $10^7$ mol $dm^{-3}$ s at pH = 4.95, t = 30° C from these values the value of inhibition parameter B was found to be **4.78 x $10^4$mol $dm^{-3}$**

**Table 2** 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 |

### 4.5 Ag(I) Catalysed Reaction

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

### 4.6 [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 °C The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in **Figure 1**

### 4.7 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 ° C in acetate buffer medium. The values of first order rate constant $k_{cat}$ for S(IV) oxidation was determine are shown in **Figure 2**. The nature of dependence of $k_{cat}$ on Ag (I) was indicated as two term rate law (6)

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

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

From the plot in **Figure2** 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 $dm^{-3}$srespectively at pH = 4.95, t = 30 °C, in acetate buffered medium.

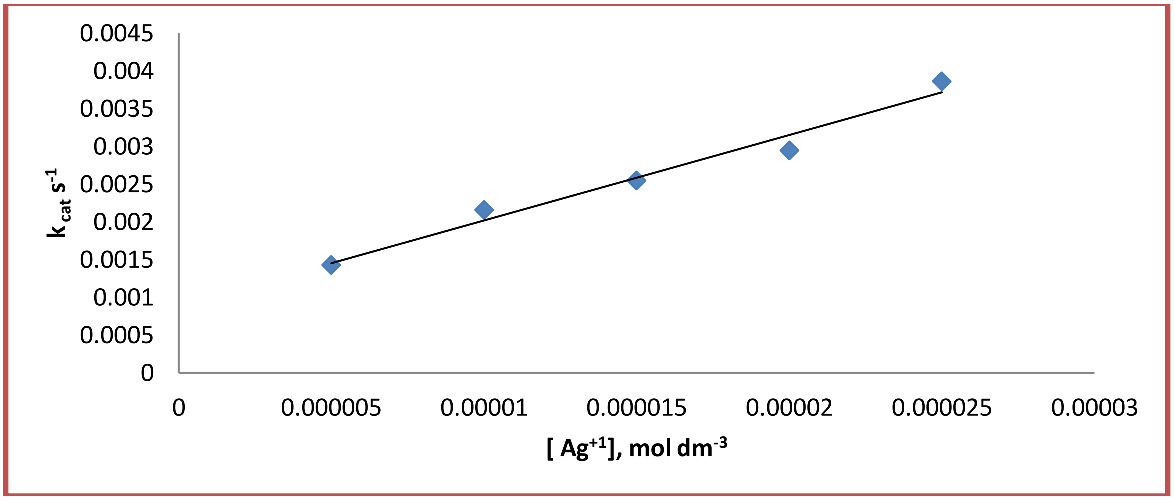

**Figure 2 The dependence of catalyst concentration at [S(IV)] = $2x10^{-3}$ mol $dm^{-3}$,pH = 4.95, t = 30 °C in acetate buffered medium**

### 4.8 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 **Figure 3**

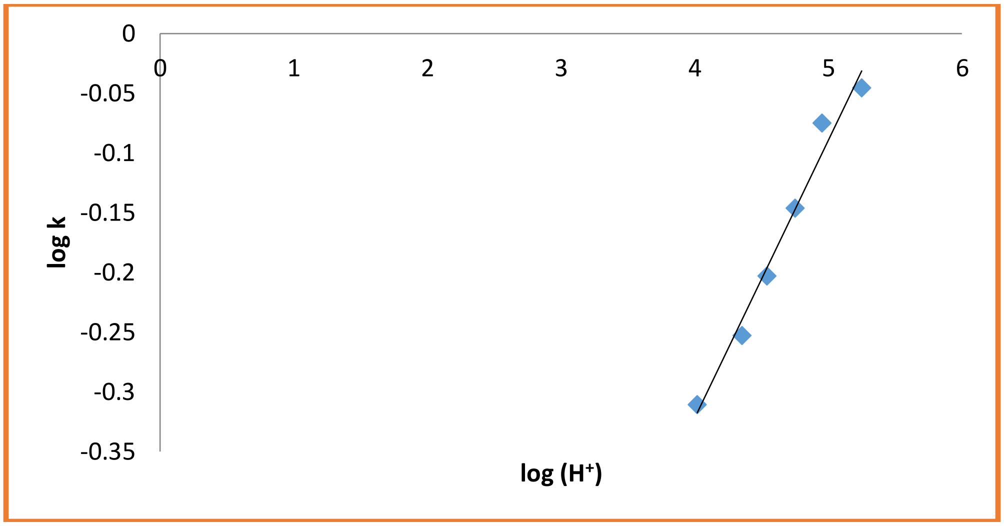

**Figure 3Effect of pH at [S(IV)] = $2x10^{-3}$ mol $dm^{-3}$ Ag (I) = $5x10^{-6}$ mol $dm^{-3}$,[Benzamide] = $7.0x10^{-7}$ mol $dm^{-3}$, t= $30^{o}$ C in acetate buffered medium**.

**Table 3 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 $10^{-3}$ | 0.733 x $10^{-3}$ | 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 4 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** |

### 4.9 [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 $x10^{-4}$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

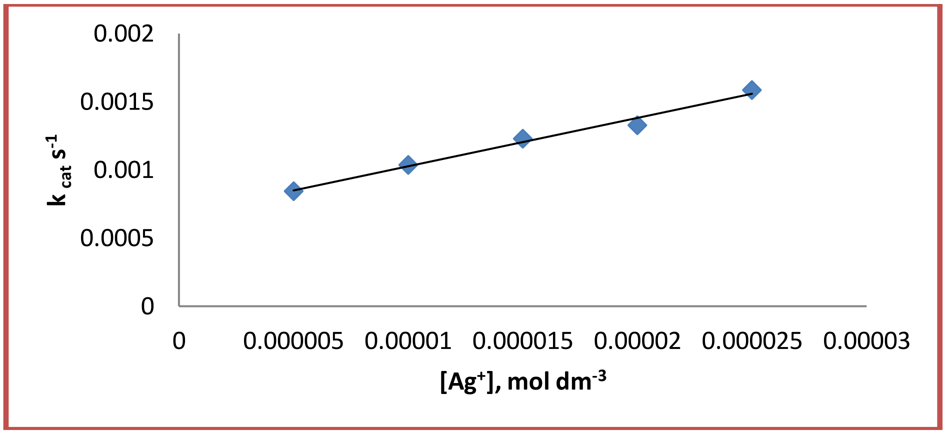

**Figure4**Effect of catalyst at [S(IV)] = 2x10$^{-3}$ mol dm$^{-3}$,[Benzamide] = 7.0x10$^{-7}$ mol dm$^{-3}$, t= 30$^o$C in acetate buffered medium. The value of intercept and slope are 6.7 x 10$^{-4}$ s and3.5 x 10$^1$ mol dm$^{-3}$ s respectively. Depending on the observed results the reaction follows the following rate law (8)

-d [S(IV)] /dt = $(k_1+k_2[Ag(I)]\ [S(IV)] / 1 + B\ [Benzamide]$ (8)
Where $k_{inh}$ = $(k_1+k_2[Ag(I)] / 1 + B\ [Benzamide] = k_{cat}/ 1 + B\ [Benzamide]$ (9)
$1/k_{inh=} 1 + B\ [Benzamide] / k_{cat}$ (10)
$1/\ k_{inh}\ =\ 1/ k_{cat}\ +\ B\ [Benzamide] /\ k_{cat}$ (11)

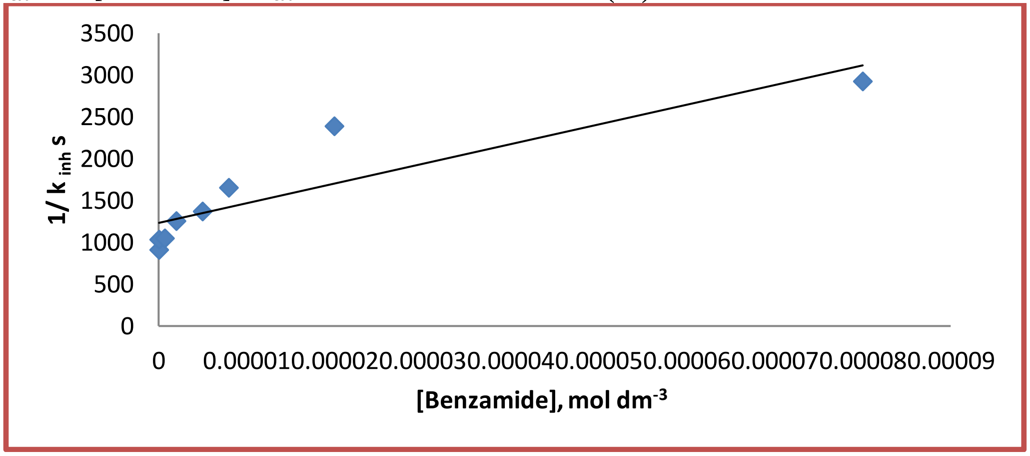

**Figure5**Effect of benzamide at [S(IV)] = 2x10$^{-3}$ mol dm$^{-3}$,Ag (I) = 5x10$^{-6}$ mol dm$^{-3}$,pH = 4.95, t = 30$^o$C in acetate buffered medium. The plot of 1/ $k_{inh}$v/s [Benzamide] is linear with intercept 1.23 x 10$^3$s and slope 2.35 x 10$^7$mol dm$^{-3}$ s from which the value of **B = 1.91 x10$^4$ mol dm$^{-3}$**

### 4.1 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**by plotting a graph between log k v/s 1/Tyield us an apparent empirical energy of activation 17.05 KJ mol$^{-1}$

**Table 5Effect 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 $10^{-4}$ $moldm^{-3}$,pH = 4.95**

| $t^oC$ | $10^3 k_{obs} s^{-1}$ |
|---|---|
| 30 | 0.842 |
| 35 | 0.924 |
| 40 | 1.01 |

## 5. 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)[18]. Prasad et al studied the inhibiting effect of isoamyl alcohol (2015)[19] formic acid, (2015)[20] isopropyl alcohol,(2016)[21] in the presence of Ag (I) catalysed autoxidation of S(IV) and reported the they all are influence the S(IV) oxidation in atmosphere with moderate rate. Gupta et al studied the role of some organics on the oxidation of dissolved sulfur dioxide by oxygen in rain water medium and found it follows radical mechanism so free radical scavengers such as VOCs decelerate the S(IV) oxidation and control the rain water acidity.(2014)[22] 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. Gupta et al studied the kinetics of environmentally important oxidation of S(IV) in acetate buffered medium in presence of Iron (III) in pH range 5.27- 5.70 and reported that addition of ethanol leads to decrease in reaction rate.(2008).[25] Backstrom (1934)[26] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and $O_2$. Gupta et al studied the influence of hydroxyl VOCs on the oxidation of S(IV) by oxygen and found VOCs inhibited the S(IV) oxidation(2014).[27] Bostjan et al (2006)[28] 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)[29]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 benzamideare found to be in the range $10^3$- $10^4$ 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)[30]

$$HSO_3^{-1} \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{-2} \quad K_d = 5.01 \times 10^{-7\,,\,18} \qquad (13)$$

$$Ag^+ + {}^-O_2CCH_3 \overset{K_{oAc}}{\rightleftharpoons} AgO_2CCH_3 \quad K_{oAc} = 2.29^{33} \qquad (14)$$

$$Ag^+ + SO_3^{-2} \overset{K_1}{\rightleftharpoons} AgOSO_2^- \quad K_1 = 2.51x\ 10^{5},^{29} \qquad (15)$$

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

$$AgOSO_2^- + O_2 \underset{K_4}{\overset{K_3}{\rightleftharpoons}} AgOSO_2^{-1}.O_2 \quad (17)$$

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$$AgHSO_3 + O_2 \rightleftharpoons AgHSO_{3.}O_2 \qquad (18)$$

$$AgHSO_{3.}O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \qquad (19)$$

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

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

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

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

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

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

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

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

$$SO_4^{\overline{\bullet}} + \text{sodium benzoate} \xrightarrow{k_{10}} \text{Non Chain product} \qquad (28)$$

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

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

Since the reaction is completely stopped in the presence of [Benzamide] at $8x10^{-5}$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)

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

We proposed this mechanism which is coincide with earlier worker of Gupta et al and Prasad et al for the $Co_2O_3$ and CoOcatalysed 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 $1.91 \times 10^4$ 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 $3.58 \times 10^3$ 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.

## 6. **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.

## 7. **Acknowledgement**

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Author(s) & Affiliation

**Arun Kumar Sharma*[1],Rashmi Sharma[2]and D. S. N. Prasad[1]**

[1]Physical Chemistry Laboratory,Department of Chemistry Govt. P. G. College, Jhalawar- 326001, Rajasthan (India)
[2]Physical Chemistry Laboratory,Department of Chemistry S.P.C. Govt. College, Ajmer- 305001, Rajasthan (India)