

## Research Article

## Ag (I) catalysed autoxidation of S (IV) and its inhibition by Iso propyl alcohol in acidic medium

Arun Kumar Sharma<sup>1</sup>, P. Parashar<sup>1</sup>, A.K. Gupta<sup>1</sup>, Rashmi Sharma<sup>2</sup> and D. S. N. Prasad<sup>1\*</sup><sup>1</sup>Department of Chemistry Govt. P. G. College, Jhalawar- 326001, Rajasthan (India)<sup>2</sup>Department of Chemistry S.P.S. Govt. College, Ajmer- 305001, Rajasthan (India)**Abstract**

The purpose of present work was to study the influence of Iso propyl alcohol on Ag (I) catalysed S (IV) oxidation under the conditions representatives for acidified atmospheric water. The kinetics of atmospheric autoxidation of sulphur (IV) by Ag (I) in the pH range 4.02-5.25 has been studied and based on the observed results a free radical mechanism operative and following rate law has been proposed. Hence the results are useful for modeling rain water acidity and therefore a great use of meteorology and atmospheric chemistry

**Keywords:** Kinetics; Autoxidation ; S(IV) ; Ag(I); Catalysis; Inhibition ;Iso propyl alcohol

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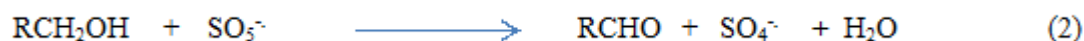
$$-d [S(IV)]/dt = (k_1+k_2[Ag]) [S(IV)] / 1 + B [Iso \text{ Propyl alcohol}]$$

**1. 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  $1.8 \times 10^{-6}$  and  $3.1 \times 10^{-7}$  M; respectively (Herrmann et al., 2000)[14]. The interaction between alcohols and the SO<sub>2</sub> 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:

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

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<sub>3</sub><sup>•-</sup>; SO<sub>4</sub><sup>•-</sup> and SO<sub>5</sub><sup>•-</sup> in the formation of a chain and to explain the previously observed alcohol inhibition by the reaction:



The interests of further researchers were focused on gaining the direct experimental evidence for the reactivity of sulphonyl radicals with respect to alcohols, which resulted in proving the unshakable ability of these compounds to react with  $\text{SO}_4^{\cdot-}$  (Ashmore, 1963; [2] Gilbert et al., 1988; [9] Dogliotti and Hayon, 1967; [8] Clifton and Huie, 1989) [5], whereas reactions with  $\text{SO}_3^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$  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., 1996, 2001; [27] Ziajka and Pasiuk-Bronikowska, 1999, 2000, 2003). [27, 28, 30] The methanol inhibition of the uncatalysed autoxidation of  $\text{HSO}_3$  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  $\text{O}_2$  in acidic medium in the presence of Iso-propyl alcohol to examine its effect on the reaction rate.

## 2. 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 an outer part for circulating thermostatic water for maintaining the desired temperature  $30 \pm 1^\circ\text{C}$ . The reaction was initiated by adding the desired volume of  $\text{Na}_2\text{SO}_3$  solution to the reaction mixture containing other additive such as buffer and catalyst. The reaction mixture was stirred continuously and magnetically at  $1600 \pm 10$  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  $10 \text{ cm}^3$  buffer made from sodium acetate ( $0.07 \text{ mol L}^{-1}$ ) and acetic acid ( $0.03 \text{ mol L}^{-1}$ ) for acidic medium were used (total volume  $100 \text{ cm}^3$ ) 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.

## 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  $\text{BaSO}_4$  using standard procedure.

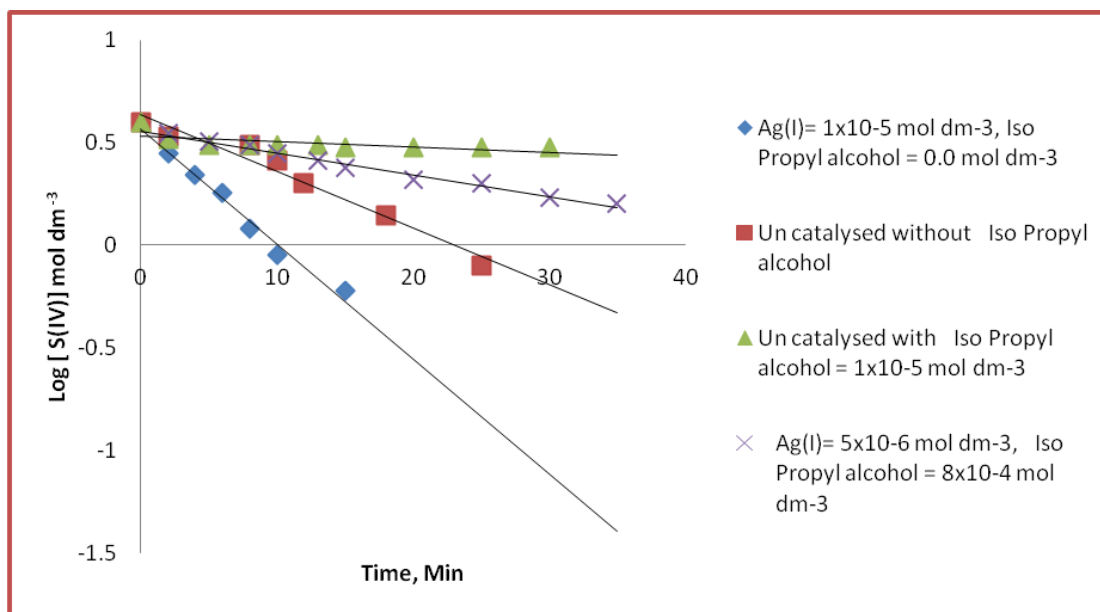
The product analysis showed the recovery of sulphate to be  $98 \pm 1\%$ ., in all cases in agreement with eq. (3)



## 4. Results

### 4.1 Preliminary Investigation -

The kinetics of both uncatalysed and Ag (I) Catalysed and Iso propyl alcohol inhibited reaction were studied in acidic medium in pH 4.95 and temperature  $30^\circ\text{C}$ . 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  $\log [\text{S(IV)}]$  versus time  $t$ . The plots were shown in **figure 1** From the **figure 1** observed that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by Iso propyl alcohol.



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

- (◇) Ag (I) =  $1 \times 10^{-5}$  mol dm<sup>-3</sup>, (Iso propyl alcohol) = 0.0 mol dm<sup>-3</sup>  
 (□) Uncatalysed without Iso propyl alcohol  
 (△) Uncatalysed with Iso propyl alcohol =  $1 \times 10^{-5}$  mol dm<sup>-3</sup>  
 (x) Ag (I) =  $5 \times 10^{-6}$  mol dm<sup>-3</sup>, (Iso propyl alcohol) =  $8 \times 10^{-4}$  mol dm<sup>-3</sup>

## 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  $1 \times 10^{-3}$  mol dm<sup>-3</sup> to  $4 \times 10^{-3}$  mol dm<sup>-3</sup> 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  $k_1$  are given in **Table 1**. The dependence of reaction rate on [S(IV)] follows the rate law (4)

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

**Table 1** The values of  $k_1$  for uncatalysed reaction at different [S(IV)] at pH = 4.95, t = 30 °C CH<sub>3</sub>COONa =  $7 \times 10^{-2}$  mol L<sup>-1</sup> CH<sub>3</sub>COOH =  $3 \times 10^{-2}$  mol L<sup>-1</sup>

[S(IV)] mol dm <sup>-3</sup>	(10 <sup>3</sup> ) k <sub>1</sub> s <sup>-1</sup>
0.001	1.04
0.002	1.06
0.003	1.09
0.004	1.09

#### 4.4 [Iso propyl alcohol] Dependence -

The major aim of this study was to examine the effect of Iso propyl alcohol on the autoxidation of S(IV) in acetate buffer medium and varying the [ Iso propyl alcohol] from  $5 \times 10^{-7}$  mol dm<sup>-3</sup> to  $8 \times 10^{-4}$  mol dm<sup>-3</sup>. We observed the rate of the reaction decreased by increasing [Iso propyl alcohol]. The results are given in Table 1.2. However, the nature of the [S(IV)] dependence in presence of Iso propyl alcohol did not change and remains first order. The first order rate constant  $k_{inh}$ , in the presence of Iso propyl alcohol was defined by rate law (5)

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

The values of  $k_{inh}$  in the presence of Iso propyl alcohol decreased with increasing [Iso propyl alcohol] are given in Table 1.2 which are in agreement with the rate law (6)

$$k_{inh} = k_1 / (1 + B [\text{Iso propyl alcohol}]) \quad (6)$$

Where B is inhibition parameter for rate inhibition by Iso propyl alcohol

The equation (4) on rearrangement becomes

$$1/k_{inh} = 1/k_1 + B [\text{Iso propyl alcohol}] / k_1 \quad (7)$$

In accordance with the equation (8) the plot of  $1/k_{inh}$  v/s [Iso propyl alcohol] 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  $1.11 \times 10^4$  s and  $5.47 \times 10^6$  mol dm<sup>-3</sup>s at pH = 4.95, t = 30 °C. From these values the value of inhibition parameter B was found to be  $4.92 \times 10^3$  mol dm<sup>-3</sup>

**Table 2** The values of  $k_{inh}$  at different [Iso propyl alcohol] at pH = 4.95, t = 30 °C  
CH<sub>3</sub>COONa =  $7 \times 10^{-2}$  mol L<sup>-1</sup> CH<sub>3</sub>COOH =  $3 \times 10^{-2}$  mol L<sup>-1</sup>

[Iso propyl alcohol] mol dm <sup>-3</sup>	$10^3 k_{inh}$ s <sup>-1</sup>	$1/k_{inh}$ s
$5.0 \times 10^{-7}$	1.17	855
$8.0 \times 10^{-7}$	1.13	885
$3.0 \times 10^{-6}$	1.08	926
$5.0 \times 10^{-6}$	0.93	1075
$1.0 \times 10^{-5}$	0.80	1250
$5.0 \times 10^{-5}$	0.77	1299
$7.0 \times 10^{-5}$	0.48	2083
$3.0 \times 10^{-4}$	0.38	2632
$8.0 \times 10^{-4}$	0.18	5556

#### 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  $1 \times 10^{-3}$  mol dm<sup>-3</sup> to  $10 \times 10^3$  mol dm<sup>-3</sup> at two different but fixed Ag(I) of  $5 \times 10^{-6}$  mol dm<sup>-3</sup> and  $1 \times 10^{-5}$  mol dm<sup>-3</sup> 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

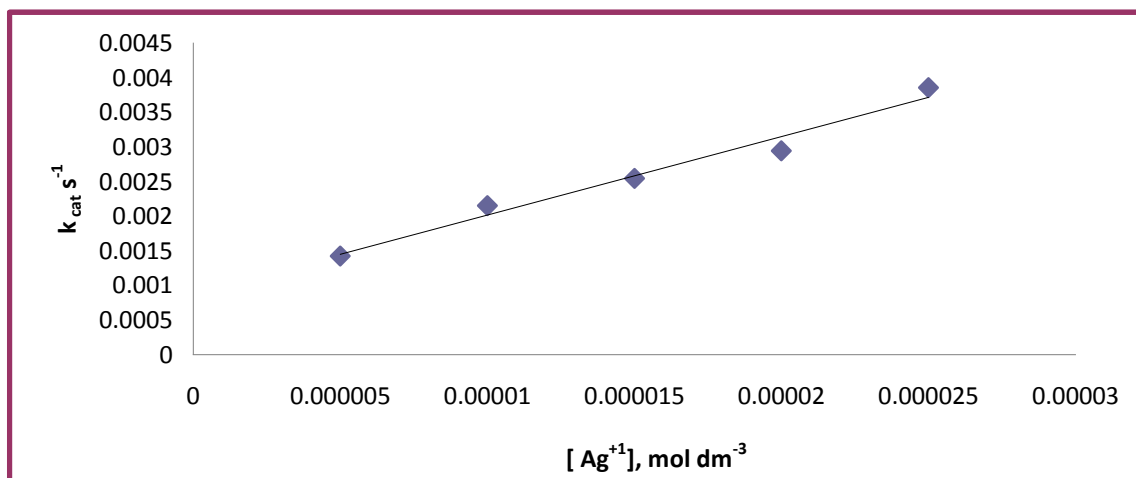
The dependence of Ag(I) on the reaction rate was studied by varying Ag(I) from  $5 \times 10^{-6}$  mol dm<sup>-3</sup> to  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> at S(IV) =  $2 \times 10^{-3}$  mol dm<sup>-3</sup> pH = 4.95, t = 30 °C in acetate buffer medium. The values of First order rate constant  $k_{cat}$

for S(IV) oxidation was determined are shown in fig 1.2. The nature of dependence of  $k_{cat}$  on Ag (I) was indicated as two term rate law – (8)

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

$$\text{Or } k_{cat} = k_1 + k_2[Ag(I)] \quad (9)$$

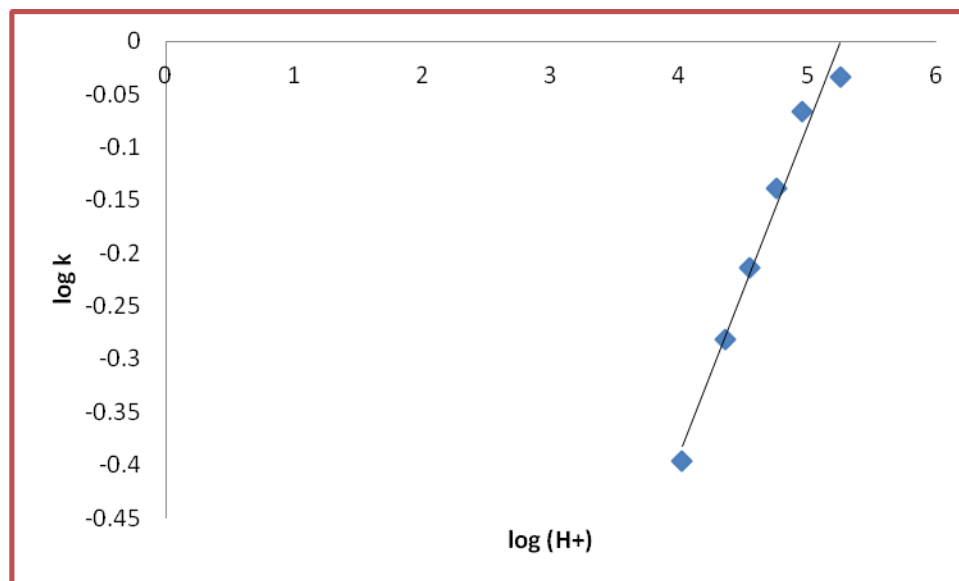
From the plot in fig 1.3 the values of intercept is equal to  $k_1$  and slope is equal to  $k_2$  were found to be  $0.72 \times 10^{-1} \text{ s}$  and  $8.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}$  respectively at  $\text{pH} = 4.95$ ,  $t = 30^\circ\text{C}$ , in acetate buffered medium.



**Figure 2** The dependence of catalyst concentration at  $[S(IV)] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} = 4.95$ ,  $t = 30^\circ\text{C}$ , in acetate buffered medium

#### 4.8 Variation of pH –

Variation of pH was carried out from 4.02- 5.25 at different  $[S(IV)]$ ,  $Ag(I)$ , [Iso propyl 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 1.3



**Figure 1.3** Effect of pH at  $[S(IV)] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $Ag(I) = 5 \times 10^{-6} \text{ mol dm}^{-3}$ , [Iso propyl alcohol] =  $7.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $t = 30^\circ\text{C}$  in acetate buffered medium

**Table 1.3** Rate of Ag (I) catalysed autoxidation in the presence of Iso propyl alcohol

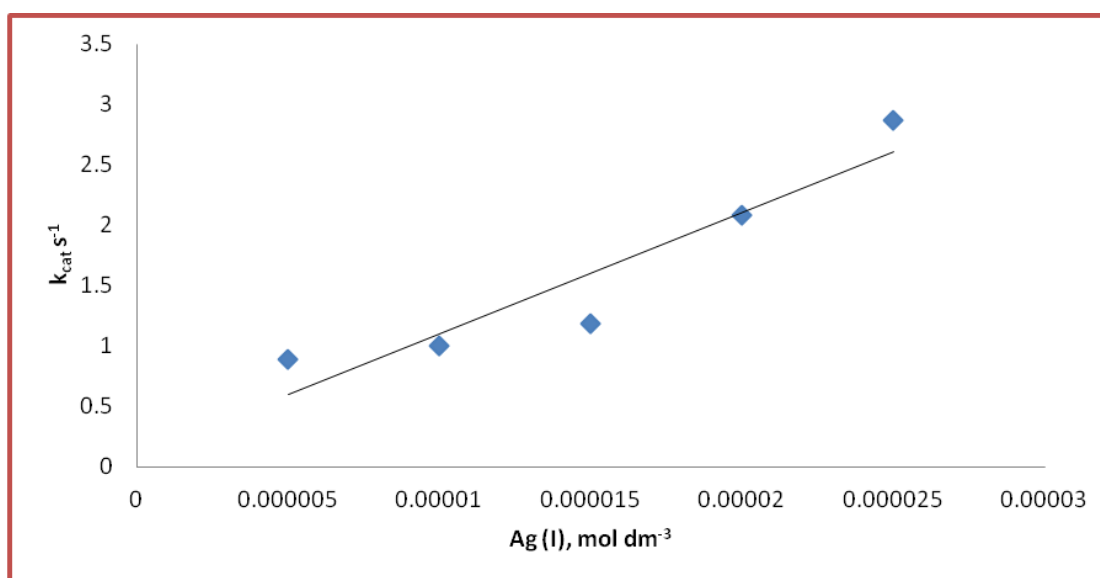
[Iso propyl alcohol], mol dm <sup>-3</sup>	Ag (I) =5x10 <sup>-6</sup> dm <sup>-3</sup>	mol	Ag (I) =1 x 10 <sup>-5</sup> mol dm <sup>-3</sup>	Ag (I) =1.5 x 10 <sup>-5</sup> mol dm <sup>-3</sup>	mol
pH = 4.02					
7.0 x 10 <sup>-5</sup>	0.401 x 10 <sup>-3</sup>		0.569 x 10 <sup>-3</sup>	0.670 x 10 <sup>-3</sup>	
3x 10 <sup>-4</sup>	0.264 x 10 <sup>-3</sup>		–	–	
8 x 10 <sup>-4</sup>	0.170 x 10 <sup>-3</sup>		–	–	
pH = 4.5					
7.0 x 10 <sup>-5</sup>	0.611 x 10 <sup>-3</sup>		0.722 x 10 <sup>-3</sup>	0.860 x 10 <sup>-3</sup>	
3x 10 <sup>-4</sup>	0.407 x 10 <sup>-3</sup>		–	–	
8 x 10 <sup>-4</sup>	0.337 x 10 <sup>-3</sup>		–	–	
pH = 5.25					
7.0 x 10 <sup>-5</sup>	0.925 x 10 <sup>-3</sup>		1.16 x 10 <sup>-3</sup>	1.46 x 10 <sup>-3</sup>	
3x 10 <sup>-4</sup>	0.582 x 10 <sup>-3</sup>		–	–	
8 x 10 <sup>-4</sup>	0.430 x 10 <sup>-3</sup>		–	–	

**Table 1.4** Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of Iso propyl alcohol

[Iso propyl alcohol] 7.0 x 10 <sup>-5</sup> mol dm <sup>-3</sup>	Ag (I) =5x10 <sup>-6</sup> dm <sup>-3</sup>	mol	Ag (I) =1 x 10 <sup>-5</sup> mol dm <sup>-3</sup>	mol	Ag (I) =1.5 x 10 <sup>-5</sup> mol dm <sup>-3</sup>	mol
pH = 4.5						
	<b>2.49</b>		<b>2.97</b>		<b>2.18</b>	

#### 4.9 [Iso propyl alcohol] Dependence-

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



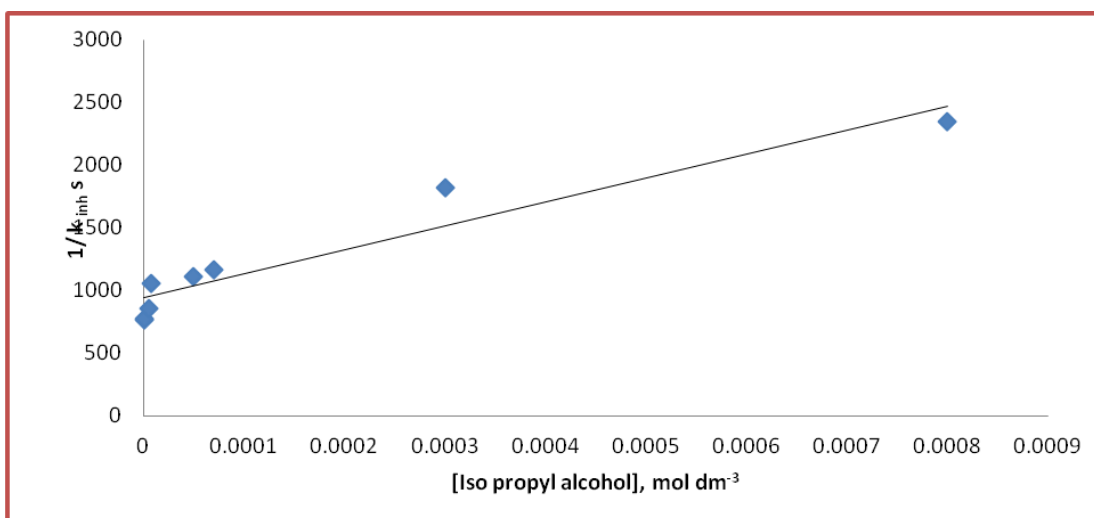
**Figure 1.4** Effect of catalysts at [S(IV)] = 2x10<sup>-3</sup> mol dm<sup>-3</sup> (Iso propyl alcohol)= 7.0x10<sup>-5</sup> mol dm<sup>-3</sup>, t= 30 °C in acetate buffered medium. The value of intercept and slope are 2.22 x 10<sup>-4</sup> s and 8.5 x 10<sup>1</sup> mol dm<sup>-3</sup> s respectively. Depending on the observed results the reaction follows the following rate law (10)

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

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

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

$$1/k_{inh} = 1/k_{cat} + B(\text{Iso propyl alcohol})/k_{cat} \quad (13)$$



**Figure 1.5** Effect of Iso propyl alcohol at  $[S(IV)] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[Ag(I)] = 5 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $\text{pH} = 4.95$ ,  $t = 30^\circ\text{C}$ , in acetate buffered medium. The Plot of  $1/k_{inh}$  v/s  $[Iso \text{ propyl alcohol}]$  is linear with intercept  $9.41 \times 10^2 \text{ s}$  and slope  $1.9 \times 10^6 \text{ mol dm}^{-3} \text{ s}$  from which the value of  $B = 2.03 \times 10^3 \text{ mol dm}^{-3}$

#### 4.10 Effect of temperature

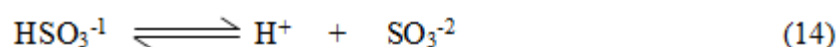
The values of  $k_{obs}$  were determined at three different temperatures in the range of  $30^\circ\text{C}$  to  $40^\circ\text{C}$ . The results are given in Table 1.5. By plotting a graph between  $\log k$  v/s  $1/t$  yield us an apparent empirical energy of activation  $71.83 \text{ KJ mol}^{-1}$

**Table 1.5** Effect of temperature  $k_{obs}$  air saturated suspensions at  $[S(IV)] = 2 \times 10^{-3} \text{ mol dm}^{-3}$  at  $[Ag(I)] = 5 \times 10^{-6} \text{ mol dm}^{-3}$   $[Iso \text{ propyl alcohol}] = 7.0 \times 10^{-5} \text{ mol dm}^{-3}$   $\text{pH} = 4.95$

$t^\circ\text{C}$	$10^3 k_{obs} \text{ s}^{-1}$
30	0.88
35	1.13
40	1.73

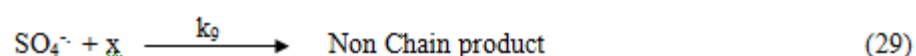
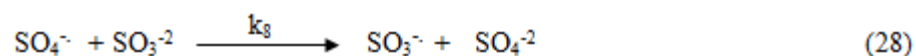
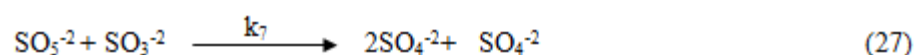
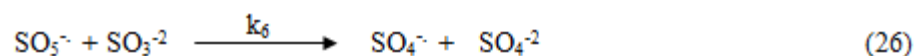
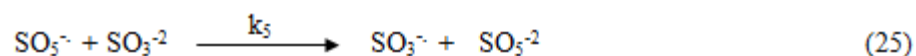
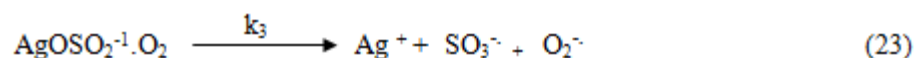
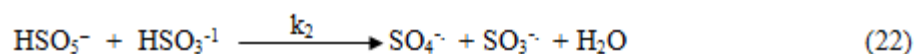
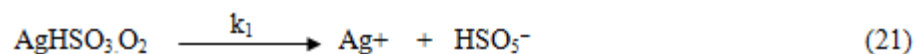
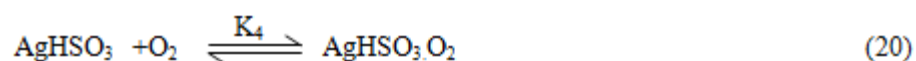
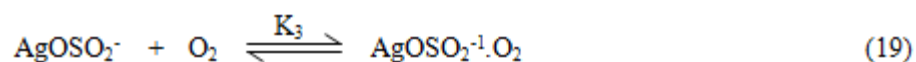
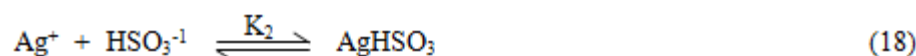
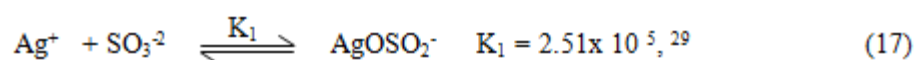
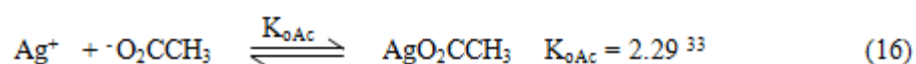
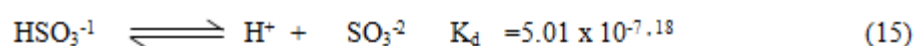
## 5. Discussion

In aqueous solutions  $\text{SO}_2$  is present in four forms  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^{-1}$ ,  $\text{SO}_3^{-2}$ ,  $\text{S}_2\text{O}_3^{-2}$  In the experimental range of pH the following equilibrium operates



The equilibrium constant is  $5.07 \times 10^{-7}$  In the experimental range of pH both species  $\text{HSO}_3^{-1}$ ,  $\text{SO}_3^{-2}$  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 – Wilkkoš [15] Bigelow et al (1898)[4] studied the effect of alcohols on the reactions between Sodium sulphite and  $\text{O}_2$  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<sub>2</sub>. Grgic et al (1998)[10] studied the inhibition effect of Acetate, Oxalate, Formate on Fe-catalysed autoxidation of S (IV) at pH 2.8, 3.7, 4.5 and found that oxalate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe<sup>+3</sup> due to formation of complex with oxalate. Bostjan et al (2006) [19] 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 Iso propyl 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<sup>-3</sup>- 10<sup>4</sup> In the present study the value of inhibition parameter for uncatalysed and Ag (I) catalysed autoxidation of S (IV) by Iso propyl alcohol are found to be 4.92 x 10<sup>-4</sup> mol dm<sup>-3</sup> and 2.03 x 10<sup>-3</sup> mol dm<sup>-3</sup> 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]



By assuming long chain hypothesis and steady state approximation  $d[\text{SO}_3^{\cdot-}]/dt$ ,  $d[\text{SO}_4^{\cdot-}]/dt$ ,  $d[\text{SO}_5^{\cdot-}]/dt$ , to zero. It can be shown that rate of initiation is equal to rate of termination. (eq. 31)



$$k_1[\text{Ag(I)}(\text{SO}_3^{2-})(\text{O}_2)] = \{k_7[\text{X}] + k_8[\text{Iso propyl alcohol}]\} [\text{SO}_4^{-1}] \quad (31)$$

Since the reaction is completely stopped in the presence of [Iso propyl alcohol] at  $8 \times 10^{-4}$  mol dm<sup>-3</sup>, so the step (26) and (29) appear to be unimportant. The step (28) is ignored because the reaction is completely seized in the presence of higher concentration of Iso propyl alcohol by omission and substitution from the above mechanism the following rate law can be obtained (32)

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

Prasad et al [22] and Gupta et al [12] proposed a similar mechanism for the Co<sub>2</sub>O<sub>3</sub> and CoO catalysed autoxidation of SO<sub>2</sub> 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  $2.03 \times 10^3$  mol dm<sup>-3</sup> which is in the range of  $10^3$  -  $10^4$  and also coincide with the reported value of B of Co<sub>2</sub>O<sub>3</sub> catalysed autoxidation of S(IV) by Iso propyl alcohol is  $3.58 \times 10^3$  mol dm<sup>-3</sup>. So on the basis of calculated value of B we concluded that Iso propyl alcohol act as a free radical scavenger in Ag(I) catalysed autoxidation of aqueous SO<sub>2</sub> 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 Iso propyl alcohol 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.

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