

## Role of Organics in Atmospheric Catalytic Autoxidation of Aqueous Sulphur Dioxide in Acidic Medium

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The kinetics of atmospheric autoxidation of sulphur(IV) by silver(I) in the pH range 4.02–5.25 was studied. The aqueous phase autoxidation of sulphur(IV) was the major factor responsible for acidification of atmospheric aqueous system. The role of organics which act as inhibitors of silver(I) catalysed autoxidation of sulphur(IV) in the acidic medium was identified and based on the observed results following rate law and a free radical mechanism was proposed:

$$d[S(IV)]/dt = (k_1 + k_2[Ag(I)]) [S(IV)]/I + B [\text{organics}].$$

Experiments were carried out at  $30 \leq t^\circ\text{C} \leq 40$ ,  $4.02 \leq \text{pH} \leq 5.25$ ,  $1 \times 10^{-3} \text{ mol/dm}^3 \leq [S(IV)] \leq 10 \times 10^{-3} \text{ mol/dm}^3$ ,  $5 \times 10^{-6} \text{ mol/dm}^3 \leq [Ag(I)] \leq 2.5 \times 10^{-5} \text{ mol/dm}^3$ ,  $1 \times 10^{-8} \text{ mol/dm}^3 \leq [\text{organics}] \leq 8 \times 10^{-4} \text{ mol/dm}^3$ . Based on the experimental results, rate constants and orders of the reactions were determined. The reaction order in sulphur(IV) was first order for both reactions in the presence and absence of organics. The effect of silver(I) ion and organics concentrations as well as an initial pH of the solution on the sulphur(IV) oxidation rate were discussed. It was found that the rate of the sulphur(IV) oxidation depended on the initial pH of the solution, but it was independent of the pH change during the reaction. The addition of organics led to the introduction of an induction period and decrease in reaction rate, most likely due to  $\text{SO}_4^{-1}$  radicals. The value of the apparent energy and inhibition constant B were calculated in the presence of organics selected as formic acid, isoamyl alcohol, sodium benzoate, benzamide, isopropyl alcohol, and aniline. Out of the six organics undertaken for study in the present work, isoamyl alcohol showed higher inhibiting capacity as compared to other five organics. The order of inhibition of selected organics are as aniline < isopropyl alcohol < formic acid < sodium benzoate < benzamide < isoamyl alcohol.

**Key words:** Kinetics; autoxidation; sulphur(IV); Ag(I); catalysis; inhibition; organic compounds

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The atmospheric oxidation of aqueous  $\text{SO}_2$  referred as S(IV) by oxygen i.e. autoxidation because this reaction is major contributor to atmospheric acid precipitation and acid rain [1–2]. Nitrogen oxides are other acid rain precursors, and their atmospheric reactions generate nitrous acid which is one of the essential trace atmospheric constituents. Autoxidation of both  $\text{SO}_2$  and  $\text{HNO}_2$  in aqueous phase has been the subject of numerous

studies [3–4]. The kinetics and mechanism of the atmospheric autoxidation of aqueous  $\text{SO}_2$  have been discussed in many research papers [5–11]. The catalytic role of trace metal ion such as Fe, Mn, Cu, [12] Ag, [13] etc. has been studied and detailed mechanism proposed. The catalytic role of the following metal oxides and others have been investigated and found these are catalysed  $\text{SO}_2$  oxidation in the atmosphere.

SPM – free fall atmospheric dust [14] non-transition metal oxide such as  $\text{MnO}_2$  [15],  $\text{SiO}_2$  [16],  $\text{MgO}$  [17],  $\text{CdO}$  [18] transition metal oxide such as  $\text{Co}_2\text{O}_3$  [19],  $\text{Ni}_2\text{O}_3$  [20],  $\text{Cu}_2\text{O}$  [21], anthropogenic material such as glass [22], and ceramics [23]. The atmosphere abounds in many volatile organic compounds and polycyclic aromatic hydrocarbon and these interfere in the atmospheric oxidation of  $\text{SO}_2$ . Hence their influence on the rate of autoxidation of  $\text{SO}_2$  both catalysed and uncatalysed has been studied in details in the last two decades [24–28]. Bigelow [29] was the first to observe the inhibiting effect of alcohols such as methanol, ethanol, propanol, butanol on the rate of the reaction between sodium sulphite and oxygen. The other organics studied are organic acids by Lee and Rochelle [30], Grgic *et al.* [31], Wolf *et al.* [32]; benzene by Ziajka *et al.* [33]; toluene, naphthalene, paraffin oil by Bronikowska *et al.* [34]; alpha-pinene, and *cis* – verbenol (Ziajka *et al.* [35]).

The effect of alcohols has been studied on several catalysed S(IV) autoxidations by Gupta *et al.* in 2008 [36]. 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, so it is planned to study the kinetics of catalysed oxidation of S(IV) by  $\text{O}_2$  in acidic medium to examine the effect of organics and nature of the mechanism. For this study Ag (I) catalyst in the presence of formic acid, isoamyl alcohol, sodium benzoate, benzamide, isopropyl alcohol and aniline were considered. This study is important in understanding the mechanism of the atmospheric oxidation of S(IV) by  $\text{O}_2$  and the role of these organic compounds which acts as organics, many of which are found in the atmosphere in trace amount.

## EXPERIMENTAL

The reaction was conducted in Erlenmeyer flask, open to air and allowing the passage of atmospheric oxygen, the oxidant. The reaction flask was immersed in thermostat water bath. The reaction mixture was stirred continuously and magnetically at  $1600 \pm 10$  rpm to allow the passage

of atmospheric oxygen and to save the response from becoming oxygen mass transfer controlled. The reaction kinetics were studied in pH range 4.02–5.25. For this purpose acetate buffered medium was used. The reaction was initiated by adding the desired volume of  $\text{Na}_2\text{SO}_3$ . 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 [37].

## PRODUCT ANALYSIS

The qualitative test shows sulphate to be the 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) was estimated gravimetrically by precipitating sulphate ions as  $\text{BaSO}_4$  using the standard procedure [38].

The product analysis showed the recovery of sulphate to be  $98 \pm 1\%$ . in all cases in agreement with Equation 1:



## RESULTS

### Preliminary Investigation

The kinetics of both uncatalysed and Ag(I) catalysed and in the presence of different organics were studied in an acidic medium in pH 4.95 and temperature  $30^\circ\text{C}$ . In both the cases the first order dependence of S(IV) were observed in the kinetics data treatment for the determination of first order rate constant  $k_1$  which was carried out from  $\log [\text{S(IV)}]$  versus time,  $t$ . The plots were shown in Figures 1 and 2. From Figures 1 and 2 it is observed that both the uncatalysed and Ag(I) catalysed organics inhibited autoxidation of S(IV) reaction.

### Uncatalysed Reaction

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

### Dependence of S(IV)

The detail dependence of the reaction rate on [S(IV)] was studied by varying it in the range  $1 \times 10^{-3} \text{ mol dm}^{-3}$  to  $4 \times 10^{-3} \text{ mol dm}^{-3}$  at pH = 4.95,  $t = 30^\circ\text{C}$  in acetate buffered medium. The kinetics were found to be first order in [S(IV)] and values of  $k_1$  was calculated from  $\log [S(IV)]$  v/s time plots which were linear. The values of first order rate constant  $k_1$  are given in Table 1. The dependence of reaction rate on [S(IV)] followed the rate law (2):

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

### [Organics] Dependence

The major aim of this study was to examine the effect of organics on the autoxidation of S(IV) in acetate buffer medium and to vary the [organics] from  $1 \times 10^{-8} \text{ mol dm}^{-3}$ ; to  $8 \times 10^{-4} \text{ mol dm}^{-3}$ , we observed the rate of the reaction decreased by increasing [organics]. The results are given in Table 2. However the nature of the [S(IV)] dependence in the presence of organics did not change and remained first order. The first order rate constant  $k_{inh}$  in the presence of organics was defined by rate law (3):

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

The values of  $k_{inh}$  in the presence of organics decreased with increasing [Organics] are given

in Table 2 which was in agreement with the rate law (4):

$$k_{inh} = k_1 / (1+B [\text{Organics}]) \quad (4)$$

Where, B is inhibition parameter for rate inhibition by organics.

The Equation 4 on re-arrangement becomes:

$$1/ k_{inh} = 1/ k_1 + B [\text{Organics}] / k_1 \quad (5)$$

### Ag(I) Catalysed Reaction

At first, the kinetics of Ag(I) catalysed reaction in the absence of organics was studied.

### [S(IV)] Variation

The dependence of S(IV) on reaction rate was studied by varying [S(IV)] from  $1 \times 10^{-3} \text{ mol dm}^{-3}$  to  $10 \times 10^{-3} \text{ mol dm}^{-3}$  at two different but fixed Ag(I) of  $5 \times 10^{-6} \text{ mol dm}^{-3}$  and  $1 \times 10^{-5} \text{ mol dm}^{-3}$ , pH = 4.95,  $t = 30^\circ$ . The kinetics was found to be first order in [S(IV)] *versus* time were linear as shown in Figures 1 and 2.

### Ag (I) Variations

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

**Table 1.** The values of  $k_1$  for uncatalysed reaction at different [S(IV)] , pH = 4.95,  $t = 30^\circ\text{C}$ ,  $\text{CH}_3\text{COONa} = 7 \times 10^{-2} \text{ mol l}^{-1}$ ,  $\text{CH}_3\text{COOH} = 3 \times 10^{-2} \text{ mol l}^{-1}$

[S(IV)] mol dm <sup>-3</sup>	(10 <sup>3</sup> ) k <sub>1</sub> s <sup>-1</sup>
$1 \times 10^{-3}$	1.04
$2 \times 10^{-3}$	1.06
$3 \times 10^{-3}$	1.09
$4 \times 10^{-3}$	1.09

**Table 2.** The values of  $k_{inh}$  at different [Organics], pH = 4.95, t = 30°C  
 $CH_3COONa = 7 \times 10^{-2} \text{ mol L}^{-1}$   $CH_3COOH = 3 \times 10^{-2} \text{ mol L}^{-1}$ 

[Organics] $\text{mol dm}^{-3}$	10 ${}^3k_{\text{benzamide}}$ $\text{s}^{-1}$	10 ${}^3k_{\text{formic}}$ $\text{s}^{-1}$	10 ${}^3k_{\text{isopropylalco.}}$ $\text{s}^{-1}$	10 ${}^3k_{\text{isoamylalco.}}$ $\text{s}^{-1}$	10 ${}^3k_{\text{sodiumbenzoate}}$ $\text{s}^{-1}$	10 ${}^3k_{\text{aniline}}$ $\text{s}^{-1}$
0.00	1.05	1.05	1.05	1.05	1.05	1.05
$1.0 \times 10^{-8}$	0.728	1.05	1.05	1.05	1.04	1.04
$5.0 \times 10^{-8}$	0.697	1.04	1.05	1.04	1.02	1.03
$8.0 \times 10^{-8}$	0.672	1.04	1.04	1.04	1.00	1.02
$2.0 \times 10^{-7}$	0.613	1.03	1.03	1.00	0.919	0.982
$5.0 \times 10^{-7}$	0.597	1.01	1.02	0.958	0.863	0.940
$7.0 \times 10^{-7}$	0.569	1.00	1.00	0.901	0.714	0.827
$3.0 \times 10^{-6}$	0.521	0.98	0.93	0.855	0.647	0.707
$5.0 \times 10^{-6}$	0.464	0.76	0.90	0.688	0.553	0.607
$8.0 \times 10^{-6}$	0.303	0.57	0.85	0.422	0.505	0.513
$5.0 \times 10^{-5}$	0.180	0.38	0.80	0.212	0.426	0.418
$7.5 \times 10^{-5}$	0.26	0.26	0.77	0.190	0.326	0.360
$1.0 \times 10^{-4}$	0.19	0.19	0.48	0.162	0.276	0.284
$3.0 \times 10^{-4}$	0.15	0.15	0.38	0.091	0.086	0.189
$5.0 \times 10^{-4}$	0.07	0.07	0.18	0.044	0.045	0.138
$8.0 \times 10^{-4}$	0.03	0.03	0.02	0.02	0.023	0.075

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

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

From the plot in Figure 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 pH = 4.95, t = 30°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), [Organics] and temperatures and summarized in Table 3. The rate decreases slightly by varying pH is inverse  $H^+$  ion dependence were observed. From the plot of  $\log k_1$  versus  $\log(H^+)$  the order concerning  $H^+$  is 0.18–0.23 which is a fractional order and can be neglected. The ratio of rates for Ag(I) catalysed oxidation in the absence and the presence of organics are summarized in Table 4 and found that it was higher for isoamyl alcohol.

### [Organics] Dependence

To know the effect of organics on Ag(I) catalysed autoxidation of S(IV) organics variation were carried out from  $1 \times 10^{-8} \text{ mol dm}^{-3}$  to  $5 \times 10^{-4} \text{ mol dm}^{-3}$  at two different Ag(I) that is  $5 \times 10^{-6} \text{ mol dm}^{-3}$  and  $1 \times 10^{-5} \text{ mol dm}^{-3}$  but fixed S(IV) =  $2 \times 10^{-3} \text{ mol dm}^{-3}$  at pH= 4.95 and t = 30°C. The results indicated that by increasing organics the rate becomes decelerates. Depending on the observed results the reaction follows the following rate law 8:

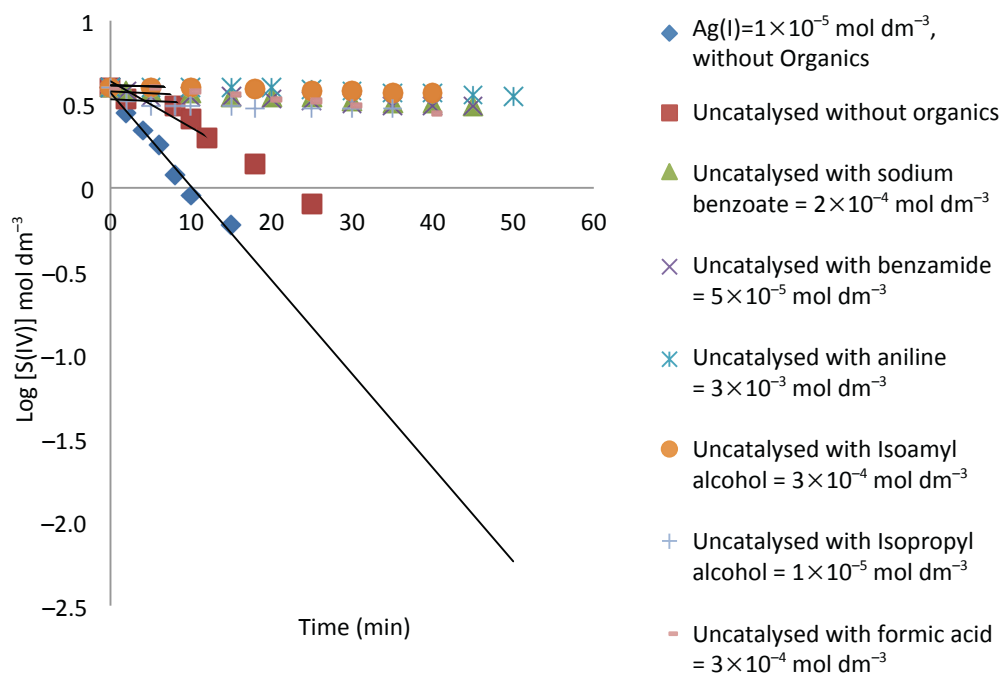
$$-d[S(IV)]/dt = (k_1 + k_2[Ag(I)])[S(IV)] / 1 + B[Organics] \quad (8)$$

$$\text{Where } k_{inh} = (k_1 + k_2[Ag(I)] / 1 + B[Organics]) = k_{cat} / 1 + B[Organics] \quad (9)$$

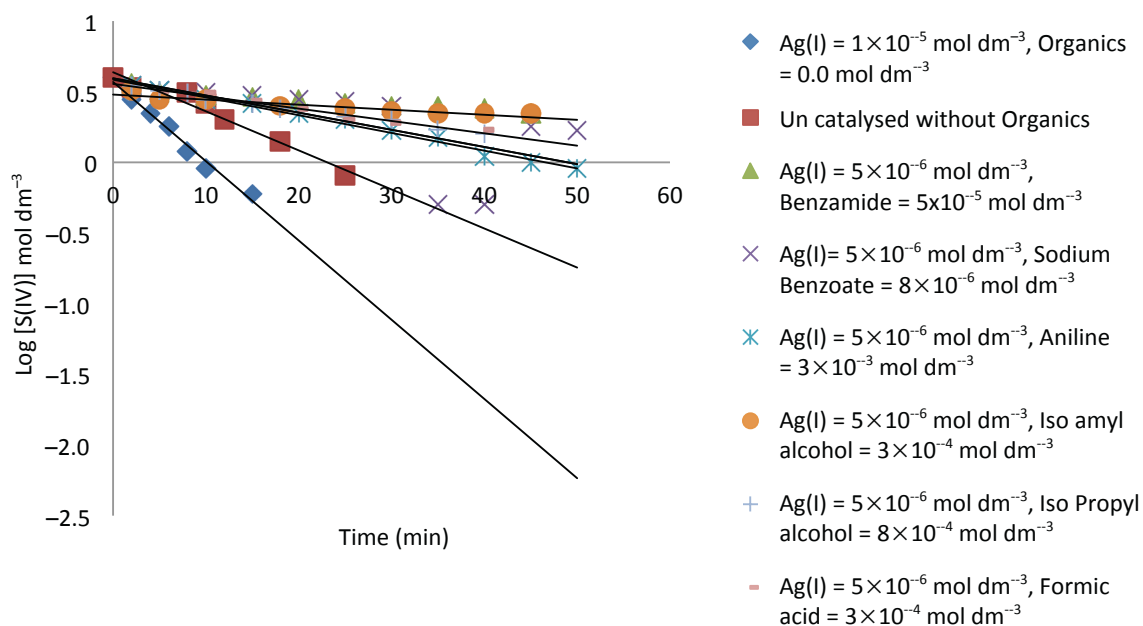
$$1/k_{inh} = 1 + B[Organics] / k_{cat} \quad (10)$$

$$1/k_{inh} = 1/k_{cat} + B[Organics] / k_{cat} \quad (11)$$

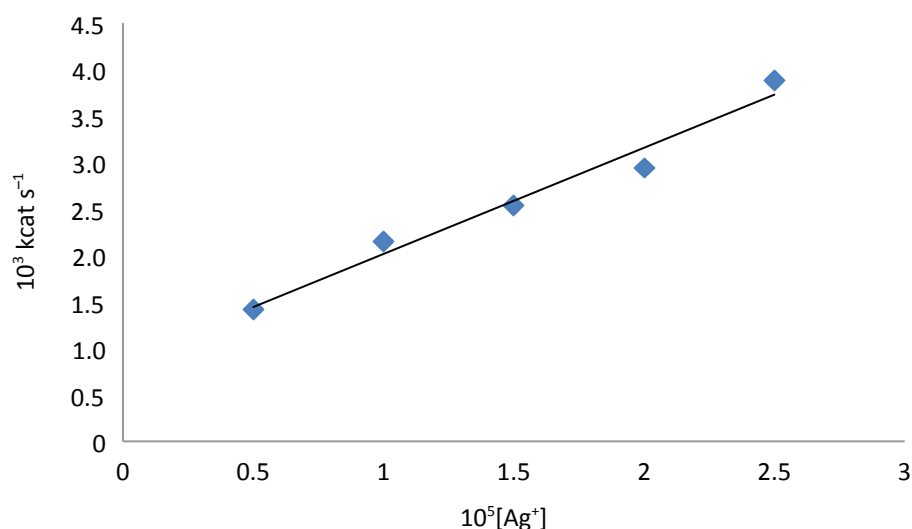
By equation we plot a graph between  $1/k_{inh}$  versus [Organics], found  $1/k_{cat}$  was the intercept and



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



**Figure 2.** The disappearance of  $[\text{S(IV)}]$  with time in air saturated suspensions at  $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{Ag(I)} = 5 \times 10^{-6} \text{ mol dm}^{-3}$  at  $\text{pH} = 4.95$ ,  $t = 30^\circ\text{C}$



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

**Table 3.** Effect of pH at  $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{Ag (I)} = 5 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[\text{Organics}] = 7.0 \times 10^{-7} \text{ mol dm}^{-3}$ ,  $t = 30^\circ\text{C}$  in acetate buffered medium

pH	$10^3 k_{\text{benzamide}} \text{ s}^{-1}$	$10^3 k_{\text{formic}} \text{ s}^{-1}$	$10^3 k_{\text{isopropylalco}} \text{ s}^{-1}$	$10^3 k_{\text{isoamylalco.}} \text{ s}^{-1}$	$10^3 k_{\text{sodiumbenzoate}} \text{ s}^{-1}$	$10^3 k_{\text{aniline}} \text{ s}^{-1}$
4.02	0.489	0.315	0.401	0.172	0.354	0.470
4.35	0.559	0.365	0.523	0.214	0.392	0.514
4.56	0.627	0.426	0.611	0.272	0.484	0.564
4.75	0.714	0.469	0.726	0.328	0.659	0.607
4.95	0.842	0.491	0.859	0.373	0.853	0.686
5.25	0.901	0.553	0.925	0.422	0.926	0.717

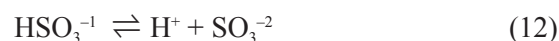
$B/k_{\text{cat}}$  was the slope so by the slope/intercept we calculated B and all the results were summarized in Table 5 by which we concluded that isoamyl alcohol had. The highest value of B which meant higher inhibition power.

### Effect of Temperature

The values of  $k_{\text{obs}}$  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 6 by plotting a graph between  $\log k$  versus  $1/t$  which yielded an apparent empirical energy of activation.

### DISCUSSION

In aqueous solutions,  $\text{SO}_2$  is present in four forms  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$ . In the experimental range of pH the following equilibrium operates, as shown in Equation 12:



The equilibrium constant is  $5.07 \times 10^{-7}$ . In the experimental range of pH both species  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$  are present but the former one present predominantly. During the course of reaction fraction order obtained is 0.18–0.23 which indicates that it is almost independent of pH

**Table 4.** Ratio of rates for Ag (I) catalysed oxidation in the absence and in the presence of Organics at pH = 4.5.

[Organics] $7.0 \times 10^{-7} \text{ mol dm}^{-3}$	Ag(I) = $5 \times 10^{-6}$ $\text{mol dm}^{-3}$	Ag(I) = $1 \times 10^{-5}$ $\text{mol dm}^{-3}$	Ag(I) = $1.5 \times 10^{-5}$ $\text{mol dm}^{-3}$
[Benzamide]	2.90	3.43	2.82
[Formic acid]	3.33	4.44	4.32
[Isopropyl alco.]	2.49	2.97	2.18
[Isoamyl alco.]	8.26	7.90	6.02
[Sodium benz.]	4.01	4.44	2.74
[Aniline]	3.01	3.81	3.54

**Table 5.** Calculated value of B (Inhibition parameter) in absence and presence of Ag(I).

Name of Organics	Inhibition parameter in the absence of Ag(I) (B) $\text{mol dm}^{-3}$	Inhibition parameter in the presence of Ag(I) (B) $\text{mol dm}^{-3}$
Formic acid	$3.33 \times 10^4$	$2.53 \times 10^3$
Sodium benzoate	$3.68 \times 10^4$	$1.48 \times 10^3$
Benzamide	$4.78 \times 10^4$	$1.91 \times 10^3$
Aniline	$1.86 \times 10^3$	$0.26 \times 10^3$
Isopropyl alcohol	$4.92 \times 10^3$	$2.03 \times 10^3$
Isoamyl alcohol	$5.07 \times 10^4$	$1.24 \times 10^4$

**Table 6.** Effect of temperature  $k_{\text{obs}}$  air saturated suspensions at  $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $\text{Ag(I)} = 5 \times 10^{-6} \text{ mol dm}^{-3}$  [Organics] =  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , pH = 4.95.

Name of Organics	Activation Energy $\text{kJ mol}^{-1}$
Formic acid	69.32
Sodium benzoate	24.11
Benzamide	17.05
Aniline	26.43
Isoamyl alcohol	71.83
Isopropyl alcohol	45.16

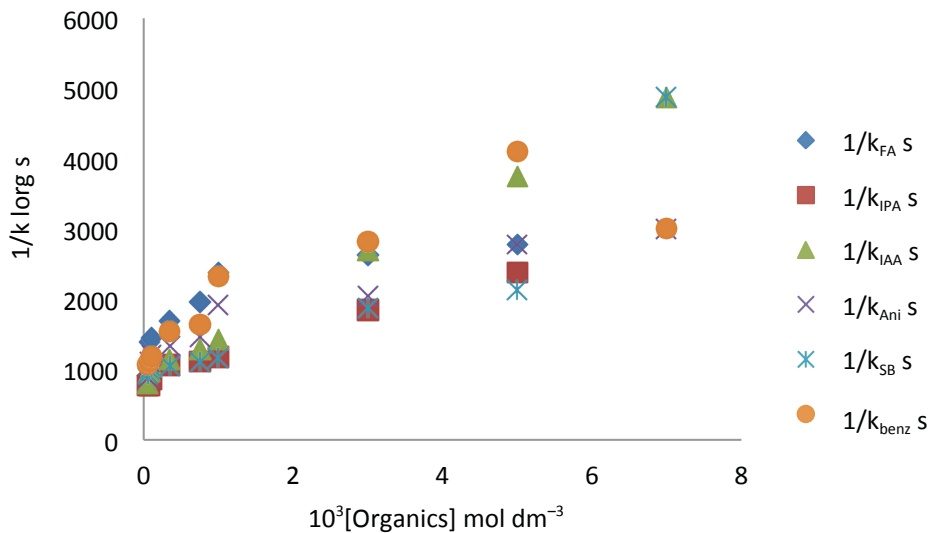
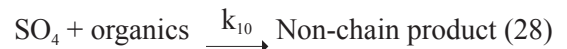
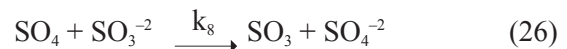
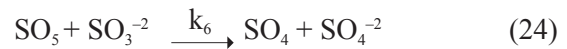
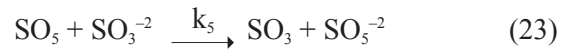
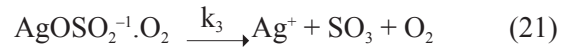
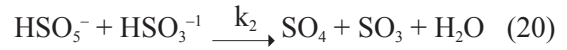
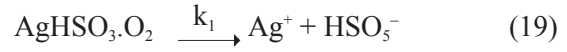
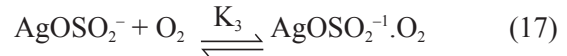
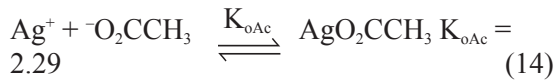
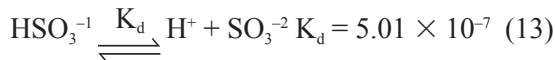
which is co-relate with the work of Wilkosz [39] Sharma *et al.* studied the inhibiting effect of formic acid [40], isopropyl alcohol [41], isoamyl alcohol [42] and aniline [43] in the presence of Ag (I) catalysed autoxidation of S(IV) and reported that these all are influence the S(IV) oxidation in the atmosphere with moderate rate.

Dayal *et al.* studied the role of some organics on the oxidation of dissolved sulphur dioxide by oxygen in rainwater 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 [44]. Grgic *et al.* studied about scavenging of  $\text{SO}_4^-$  radical anions by mono and dicarboxylic acids in the Mn (II) catalysed oxidation in aqueous solutions and reported that low molecular weight carboxylic acids have low reactivity towards sulphate radical anion [45]. Dayal *et al.* studied the influence of hydroxyl VOCs on the oxidation of S(IV) by oxygen and found VOCs inhibited the S(IV) oxidation [46],



Bostjan *et al.* [47] 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 potent inhibition. The rate of uncatalysed and Ag(I) catalysed reaction is decelerated by the addition of organics in the present study. Sameena *et al.* [48] reported that radical mechanism operate in that 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 organics are found to be in the range  $10^3 - 10^4$ . The free radical mechanism is very complex, the present work is close to the experimental condition of Connick and Zhang [49].



**Figure 4.** Effect of organics at  $[\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Ag(I)}] = 5 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $\text{pH} = 4.95$ ,  $t = 30^\circ\text{C}$  in acetate buffered medium.



By assuming long chain hypothesis and steady state approximation  $d[\text{SO}_3]/dt$ ,  $d[\text{SO}_4]/dt$ ,  $d[\text{SO}_5]/dt$ , to be zero. It can be shown that rate of initiation is equal to the rate of termination. (Equation 29)

$$k_1[\text{Ag(I)}(\text{SO}_3^{-2})(\text{O}_2)] = \{k_7[\text{X}] + k_8[\text{Organics}]\} [\text{SO}_4^{-1}] \quad (29)$$

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

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

We proposed this mechanism which coincide with earlier worker of Gupta *et al.* and Prasad *et al.* for the  $\text{Co}_2\text{O}_3$  and  $\text{CoO}$  catalysed autoxidation of  $\text{SO}_2$  inhibited by formic acid and ethanol respectively, which led to the same rate law. By comparing derived rate law with the experimental rate law we observed the similarity in these two. The calculated value of inhibition constant B is  $10^3 - 10^4 \text{ mol dm}^{-3}$  and also coincided with the reported value of B of  $\text{Co}_2\text{O}_3$  catalysed autoxidation of S(IV) by formic acid was  $3.58 \times 10^3 \text{ mol dm}^{-3}$ . So on the basis of calculated value of B we concluded that organic compounds selected for the study act as a free radical scavenger in Ag(I) catalysed autoxidation of aqueous  $\text{SO}_2$  in acidic medium and a free radical mechanism would operate in this system.

## CONCLUSIONS

The role of organics act as an inhibitor in Ag(I) catalysed autoxidation of S(IV) in the acidic medium was identified, and based on the observed results following rate law and a free radical mechanism was proposed:

- $-d [\text{S(IV)}]/dt = (k_1+k_2[\text{Ag}]) [\text{S(IV)}] / 1 + B [\text{Organics}]$  Rate law

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

Based on the experimental results, rate constant and order of the reaction were determined. The reaction order in S(IV) was first order for both reactions in the presence and absence of organics.

The effect of pH on S(IV) oxidation in the presence of Ag(I) and organics has been studied and found 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.

The effect of temperature of solution on S(IV) oxidation catalysed by Ag(I) in the presence of organics was discussed. The values of  $k_{\text{obs}}$  were determined at three different temperatures in the range between  $30^\circ\text{C}$  to  $40^\circ\text{C}$ . By plotting a graph between  $\log k$  versus  $1/t$  yielded an apparent empirical energy of activation for the reactions.

In contrast, results conclusively showed that organics studied here (Formic acid, Iso amyl alcohol, sodium benzoate, Benzamide, Iso propyl alcohol, aniline.) act as inhibitors not a catalyst for S(IV) autoxidation.

The order of inhibition of selected organics was as aniline < isopropyl alcohol < formic acid < sodium benzoate < benzamide < isoamyl alcohol.

The value of inhibition factor (B) of both uncatalysed and Ag(I) catalysed autoxidation of S(IV) in the presence of organics study was in the range of  $10^3 - 10^4$  which is coincide with earlier studies reported by Gupta *et al.* (2008) and Sameena *et al.* (2013).

Isoamyl alcohol had highest inhibiting power which might be due to the formation of more stable radicals in reaction condition used and greater abundance in the atmosphere as compare to other organics used.

The results of the study could be useful for modeling rain water acidity and therefore of great use in meteorology and atmospheric chemistry. It is also important to understanding the mechanism of the atmospheric oxidation of S(IV) by  $\text{O}_2$ .

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