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Kinetics and Mechanism of the Silver (I)-Catalyzed Autoxidation of SO_2 in Aqueous Solution and Its Inhibition by Benzoate and Amide Ions

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Abstract

In this paper we report that sodium benzoate and benzamide both are organics works as good inhibitor for SO_2 oxidation in pH range 4.02-5.25 in the presence of silver (I). Based on the observed results following rate law given and a free radical mechanism have been proposed.

$$-d\left[S\left(IV\right)\right]/dt = \left(\mathrm{k}_1 + \mathrm{k}_2\left[\mathrm{Ag}\left(\mathrm{I}\right)\right]\right)\left[\mathrm{S}\left(\mathrm{lV}\right)\right]/1 + B\ \left[organics\right]$$

Experiments were carried out at $30 \leq T°C \leq 40$, $4.02 \leq pH \leq 5.25$, 1×10^{-3}mol/dm$^3\leq$ [S(lV)$\leq 10\times10^{-3}$ mol/dm^3, 5×10^{-6}mol/dm^3 $\leq$ [Ag(I)] $\leq 2.5\times10^{-5}$mol/dm^3, 5×10^{-6}mol/dm$^3\leq$ [Sodium Benzoate]$\leq 8\times10^{4}$mol/dm^3, 5×10^{-7}mol/dm$^3\leq$ [Benzamide] $\leq 8\times10^{-4}$mol/dm^3. Rate constants and order of reaction were calculated and found pseudo- first order in all cases. The effect of pH and temperature were also discussed. The kinetic and thermodynamic parameters along with inhibition parameter have been reported. It is concluded by activation energy and inhibition values (B) is higher for benzamide, so it is better inhibitor for SO_2 inhibition compared to sodium benzoate.

Keywords: Kinetics; Autoxidation; SO_2; silver (I); Catalysis; Inhibition ; Aromatic mono carboxylic acid and aromatic amide.

1. INTRODUCTION

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[1], Sharma *et al.;* 2017 [2], Martin *et al.*; 1984[3]).
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 [4], Fuzzi, *et al.;* 1978 [5], Brimblecombe and speeding *et al.;* 1974 [6] and Hoffmann *et al.;* 1988 [7], Huss *et al.;* 1982 [8].
Mn (II) Catalysis – Wilkosz and Mainka*et al.;* 2008[9], Sharma *et al.;* 2007[10],Manoj *et al.;* 2000[11], Connick and Zhang *et al.;*1996[12], Berglund *et al.;* 1993[13], podkrajsek *et al.;* 2004[14].
Cu (II) Catalysis-Lunak *et al.*; 1978[15]. Fuller and Crist *et al.*; 1941[16].
Co(II) Catalysis-Hobson *et al.*; 1986[17], Srivastava *et al.*; 1968[18].
Ag (I) Catalysis- Gupta *et al.*; 1999[19], 2001[20]. Sharma *et al.*; 2017[21].
Ni (II) catalysis- Linn Jr *et al.*; 1990[22].

Organics are able to inhibit the oxidation of SO_2 so rain water acidity can be controlled. They increase the life span of SO_2 so vegetation, national buildings, monuments, fishes of water bodies and human being are not affected by rain water acidity. 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 mechanisms 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 Dayal *et al.*; 2014 [23-24], Meena *et al.*; 2016[25], Grigic *et al.*; 1998[26], Sharma *et al.*;2017[27-28] But still combined effect of organic compounds like sodium salt of aromatic acid and aromatic amines are not studied yet so more work is to be need in this area to understand SO_2 inhibition, Since it is planned to study the kinetics of Ag (I) catalyzed oxidation of SO_2 by O_2 in acidic medium in the presence of two organics i.e. Sodium benzoate and benzamide to examine their effect on the reaction rate. These studies are useful for modeling rain water acidity and therefore a great use of meteorology and atmospheric chemistry. This study is important in understanding the mechanism of the atmospheric oxidation of SO_2 by O_2.

2. 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 an outer part for circulating thermostatic water for maintaining the desired temperature 30 ± 1^0C. 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 was followed by withdrawing the aliquot samples periodically and titrating the unreacted SO_2iodometrically. The reproducibility of replicate measurements was generally better than 10 ± 1 %. All calculations were performed in MS Excel. Experimental set up is shown in Fig.1

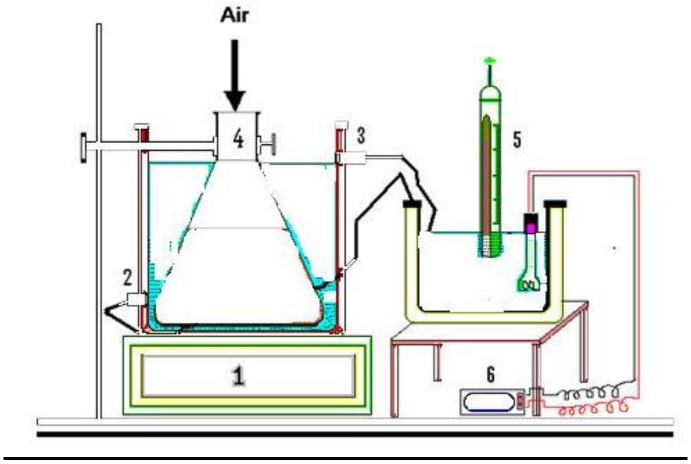

Figure 1: Schematic diagram of the experimental set up for the kinetic study of SO_2 – O_2 oxidation reaction.
1. Magnetic Stirrer,
2. Water Inlet,
3. Water outlet,
4. Erlenmeyer Flask (Reaction mixture),
5. Thermometer,
6. Thermostat.

3. PRODUCT ANALYSIS

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and SO_2in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of SO_2When the reaction was complete then S (VI) estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure [30]. The product analysis showed the recovery of sulphate to be 98±1%., in all cases in agreement with eq. (1)

$$\mathrm{S(IV)} + 0.5\,\mathrm{O_2} \longrightarrow \mathrm{S\ (VI)}. \tag{1}$$

4. RESULTS

4.1 Preliminary Investigation

The kinetics of both uncatalysed and Ag (I) catalysed, sodium benzoate and benzamide inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30°C. In all the cases the first order dependence of S (IV) was observed in the kinetics data treatment for the determination of pseudo first order rate constant $k_1$was calculated from *log [S(IV)] versus time, t*. The plots were shown in Fig 2. From the Fig 2it is observed that both the uncatalysed and silver (I).catalysed autoxidation of S (IV) reaction are inhibited bysodium benzoate and benzamide.

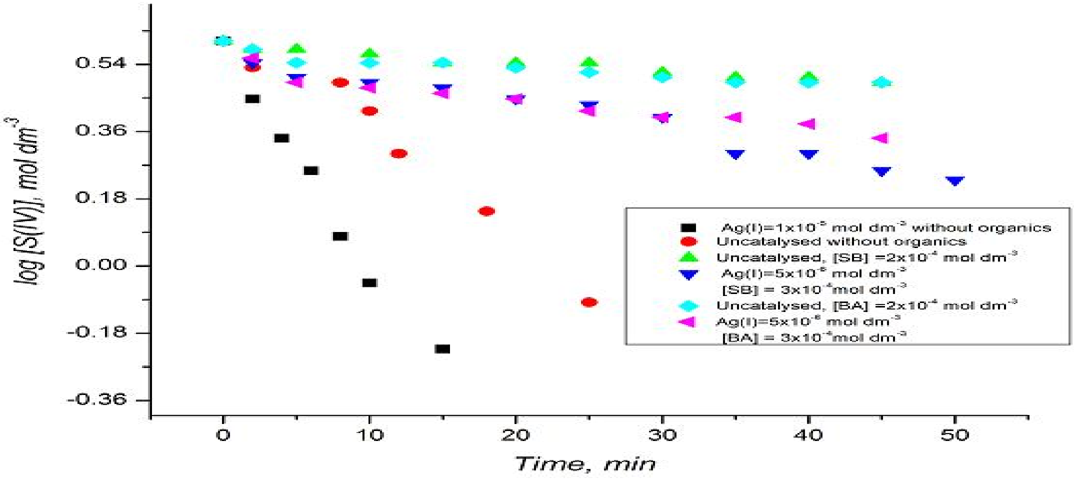

Figure 2: The disappearance of sulfur (IV) with time in air saturated suspensions at [S(IV)] = 2x10^{-3}mol dm^{-3} at pH = 4.95, t = 30°C with uncatalysed, Ag (I) catalysed, sodium benzoate and benzamide inhibited reaction.

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 SO_2oxidation 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°C in acetate buffered medium. The kinetics was found to be pseudo first order in sulfur (IV) and values of k_1 was calculated from *log [S(IV)]* v/s *time, t* plots which was linear. The value of first order rate constant $k_1$are given in Table- 1 The dependence of reaction rate on SO_2 oxidation follows the rate law (2)

$$-d\,[\mathrm{S(IV)}]\,/dt = k_1\ [\mathrm{S(IV)}]. \tag{2}$$

Table 1: The values of k_1 for uncatalysed reaction at different sulfur (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

4.4 [Organics] Dependence

The major aim of this study was to examine the effect of sodium benzoate and benzamide which are known as organics on the autoxidation of SO_2 in acetate buffer medium and varying the [Organics] from $8x10^{-8}$mol dm^{-3} to $2x10^{-4}$mol dm^{-3} we observed the rate of the reaction decreased by increasing [Organics]. However the nature of the SO_2oxidation dependence in presence of organics did not change and remains pseudo first order. The pseudo first order rate constant k_{inh}, in the presence of organics was defined by rate law (3)

$$-d\left[S(IV)\right] / dt = k_{inh}\left[S(IV)\right]. \tag{3}$$

The values of k_{inh} in the presence of organics decreased with increasing [organics] which are in agreement with the rate law (4).

$$k_{inh} = k_1 / (1+B\,[organics]) \tag{4}$$

Where *B* is inhibition parameter for rate inhibition by organics

The equation (4) on rearrangement becomes

$$1/ k_{inh} = 1/ k_1 + B\,[organics] / k_1 . \tag{5}$$

In accordance with the equation (5) the plot of $1/ k_{inh}$ v/s [organics] was found to be linear with non- zero intercept (Fig.3) The values of intercept $(1/ k_1)$and slope (B/ k_1) were found to be $1.29x10^3$mol dm^{-3}s and $4.76x10^6$ s at pH = 4.95, t = 30°C. From these values the value of inhibition parameter *B* was found to be $3.68x10^4$ mol $dm^{-3}$for sodium benzoate. The values of intercept and slope were found to be 1.68 x 10^3 s and 8.06 x 10^7mol 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 10^4mol $dm^{-3}$for benzamide.

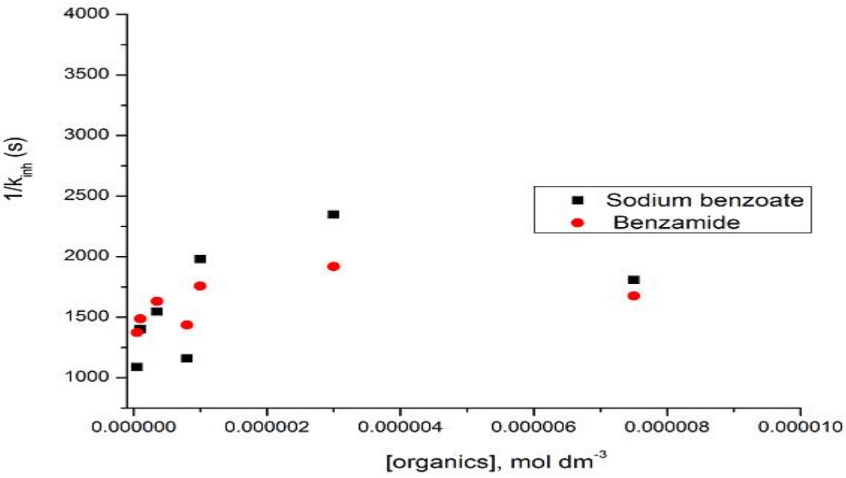

Figure 3: The plot of k_{inh}v/s [Organics] at pH = 4.95, t = 30°C, $CH_3COONa = 7x10^{-2}$ mol L^{-1} $CH_3COOH=$ $3x10^{-2}$mol L^{-1}.

4.5 Silver (I) Catalysed Reaction

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

4.6 [S (IV) Variations

The dependence of S (IV) on reaction rate was studied by varying $SO_2$from 1×10^{-3}mol dm^{-3} to 10×10^{-3}mol dm^{-3} at two different but fixed Ag(I) of 5×10^{-6}mol dm^{-3}and 1×10^{-5}mol dm^{-3} at pH = 4.95, t = 30 ° The kinetics was found to be first order in *[S(IV)] v/s time t* were linear.

4.7 Silver (I) variations

The dependence of Ag(I) on the reaction rate was studied by varying silver (I)from 5×10^{-6}mol dm^{-3} to 2.5×10^{-5}mol dm^{-3} at S(IV) = 2×10^{-3}mol dm^{-3} pH= 4.95, t= 30 ° C in acetate buffer medium. The values of first order rate constant k_{cat} for SO_2 oxidation was determine are shown in Fig- 4 The nature of dependence of k_{cat} on silver (I) was indicated as two term rate law (6)

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

$$k_{cat} = k_1+k_2\ [Ag(I)]. \tag{7}$$

From the plot in Fig.4 the values of intercept is equal to k_1 and slope is equal tok_2 were found to be 0.72x 10 ^{1} s and 8.6 x 10 $^{-3}$ mol dm^{-3} srespectively at pH = 4.5, t = 30 °C, in acetate buffered medium. Similarly dependence of k_{cat} on silver (I) were done on different concentration of organics confirmed the pseudo first order kinetics Fig.5

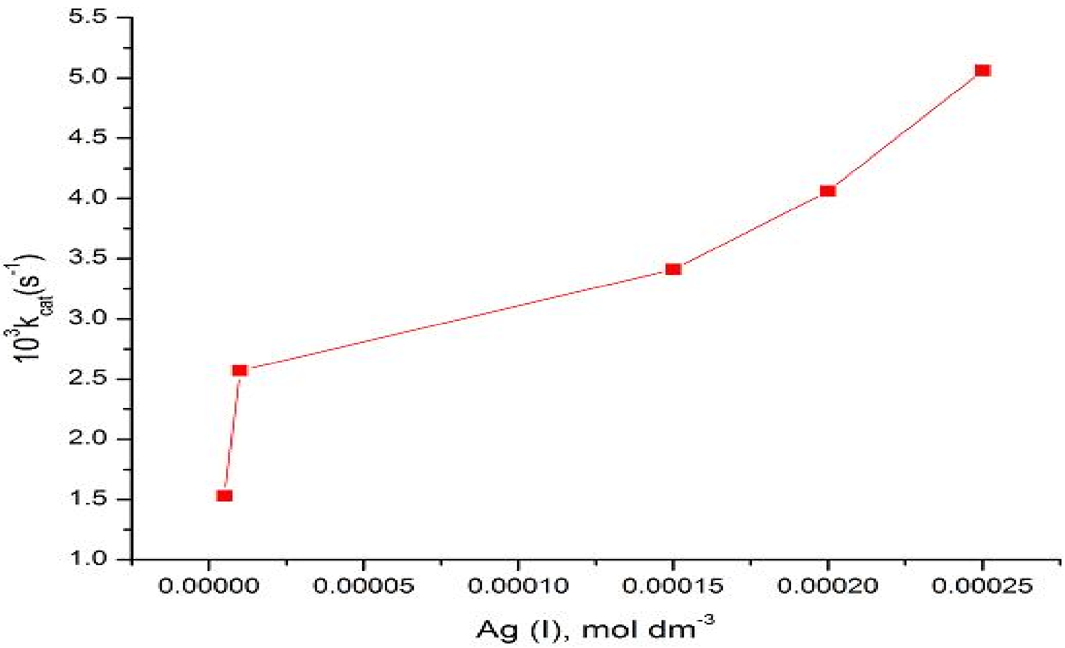

Figure 4: The dependence of catalyst concentration at [S (IV)] = 2×10^{-3} mol dm^{-3} pH = 4.95, t = 30 °C, in acetate buffered medium.

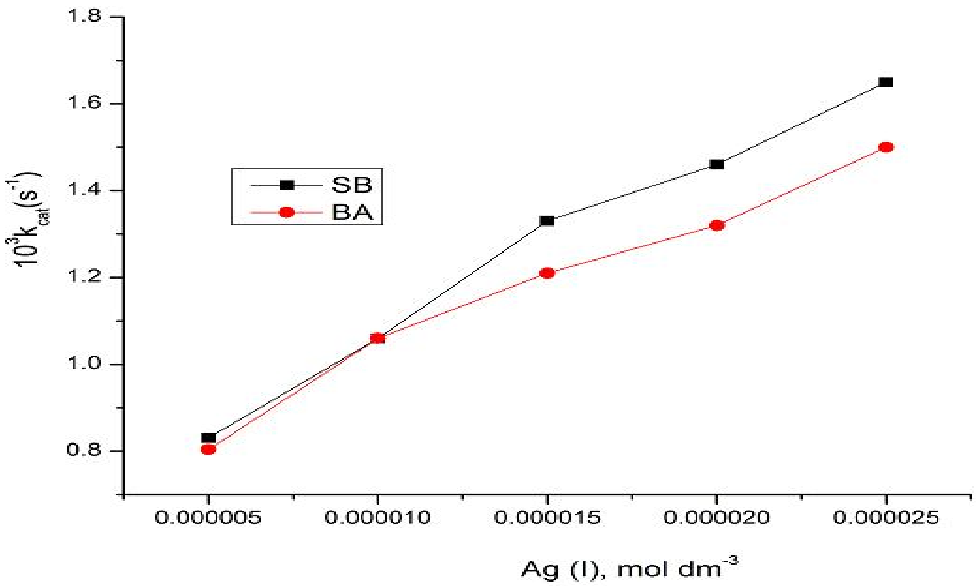

Figure 5: Effect of catalyst at [S (IV)] = $2x10^{-3}$ mol dm^{-3} (Sodium Benzoate)= $8.0x10^{-6}$mol dm^{-3}, [Benzamide]= $7.0x10^{-7}$mol dm^{-3} pH= 4.95 t= 30°C in acetate buffered medium.

4.8 Variation of pH

Variation of pH was carried out from 4.02- 5.25 at different sulfur (IV), Ag (I),[sodium benzoate], [Benzamide] and temperatures. The rate decreases slightly by varying pH is inverse H^+ ion dependence was observed. It is observed that rate of reaction depends upon initial pH but doesn't change during course of entire reactionas shown in Table 2.

Table 2: Rate of Ag (I) catalysed autoxidation in the presence of [sodium benzoate], [Benzamide]

[Sodium benzoate], mol dm^{-3}	Ag (I) =$5x10^{-6}$ mol dm^{-3}	[Benzamide] mol dm^{-3}	Ag (I) =5 x 10^{-6}mol dm^{-3}
pH = 4.02			
8.0 x 10^{-6}	0.354 x 10^{-3}	7.0 x 10^{-7}	0.489 x 10^{-3}
5.0x 10^{-5}	0.266 x 10^{-3}	7.0x 10^{-6}	0.316 x 10^{-3}
2.0 x 10^{-4}	0.183 x 10^{-3}	8.0 x 10^{-5}	0.248 x 10^{-3}
pH = 4.50			
8.0 x 10^{-6}	0.535 x 10^{-3}	7.0 x 10^{-7}	0.513 x 10^{-3}
5.0x 10^{-5}	0.318 x 10^{-3}	7.0x 10^{-6}	0.478 x 10^{-3}
2.0 x 10^{-4}	0.301 x 10^{-3}	8.0 x 10^{-5}	0.419 x 10^{-3}
pH = 5.25			
8.0 x 10^{-6}	0.626 x 10^{-3}	7.0 x 10^{-7}	0.653 x 10^{-3}
5.0 x 10^{-5}	0.509 x 10^{-3}	7.0x 10^{-6}	0.625 x 10^{-3}
2.0 x 10^{-4}	0.468 x 10^{-3}	8.0 x 10^{-5}	0.544 x 10^{-3}

4.9 [Organics] Dependence

To know the effect of sodium benzoate and benzamide on Ag (I) catalysed autoxidation of SO_2 sodium benzoate variation was carried out from $8x10^{-7}$ mol dm^{-8} to 2 x 10^{-4}mol $dm^{-3}$and benzamide variation was from $1x10^{-8}$mol dm^{-3} to 5 x 10^{-3}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 temp 30 ° C. The results indicated that by increasing organics the rate becomes decelerates (Fig.6)

Depending on the observed results the reaction follows the following rate law (8)

$$-\mathrm{d}\left[\mathrm{S(IV)}\right] / \mathrm{dt} = (k_1 + k_2\left[\mathrm{Ag(I)}\right] \left[\mathrm{S(IV)}\right] / 1 + B \left[organics\right] \quad (8)$$

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

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

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

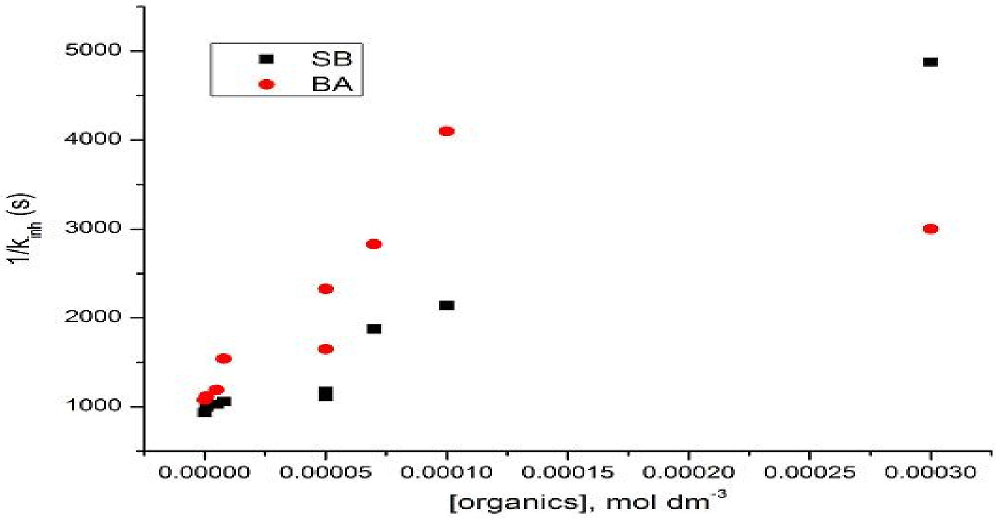

Figure 6: Effect of organics at [S(IV)] = $2x10^{-3}$ mol dm^{-3} Ag (I) = $5x10^{-6}$ mol dm^{-3} pH = 4.95, t = 30°C, in acetate buffered medium. From this graph the value of B_{SB} and B_{BA} are found as1.48 x 10^4mol $dm^{-3}$and 1.91 $x10^4$ mol dm^{-3} respectively.

4.10 Effect of temperature

The values of k_{obs} were determined at three different temperatures in the range of 30°C to 40°C. By plotting a graph between *log k v/s 1/t* yield a slope and intercept which gives an apparent empirical energy of activation *(E_a)* and frequency factor *(Z)* respectively shown in Fig. 7 and Table-3.The entropy of activation *(ΔS),* enthalpy of activation *(ΔH)* and free energy of activation *(ΔG)* were calculated using the following equation:

$$\Delta S = 2.303 \log\left(\frac{Zh}{kT}\right) R$$

$$\Delta H = E - RT$$

$$\Delta G = \Delta H - T\Delta S$$

Where k and h are the Boltzmann and Planck constants, respectively. This reaction have negative entropy, which indicates that it proceed with a lower rate than the normal ones. The negative value of entropy also indicates that the activated complex have a more ordered and more rigid structure than the reactants or intermediates. The negative values of the entropies of activation are compensated by the values of enthalpies of activation, leading to almost the same values for the free energy of activation.

Table 3: Kinetic and thermodynamic parameters for the reaction of SO_2 autoxidation

organics	**E_a (kJ mol^{-1})**	**Z (s^{-1})**	**ΔS* (J K^{-1} mol^{-1})**	**ΔH* (kJ mol^{-1})**	**ΔG* (kJ mol^{-1})**
Sodium benzoate	33.12	$4.51x10^{-5}$	-331.54	24.57	172.76
Benzamide	40.56	$3.68x10^{-2}$	-275.30	32.46	148.92

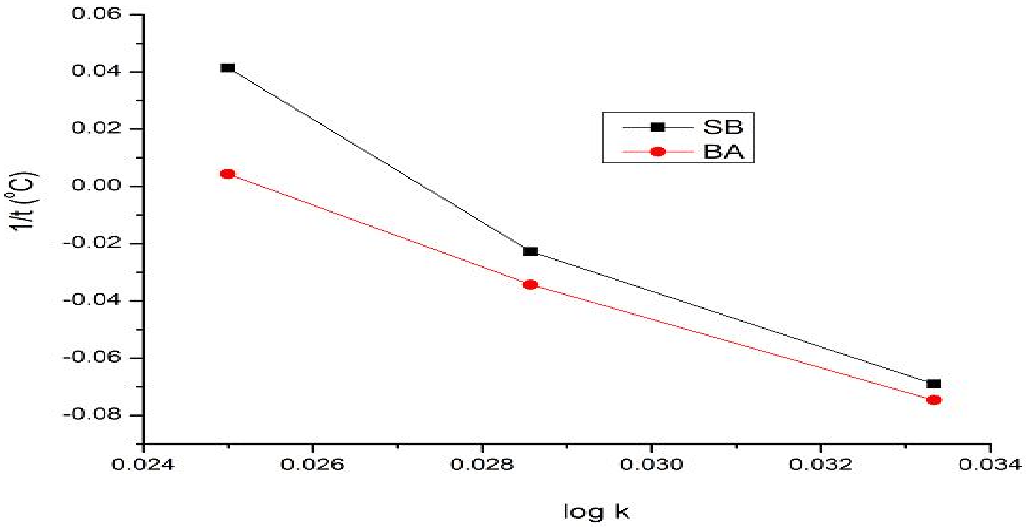

Figure 7: Effect of temperature on k_{obs}air saturated suspension at [S(IV)] = 2x10^{-3} mol dm^{-3} [organics] = 7.5 x10^{-5} mol dm^{-3}, pH = 4.95, Ag(I) = 5x10^{-6} mol dm^{-3}

Table 4: Calculated value of B (Inhibition parameter) in absence and presence of silver (I)

Name of Organics	**Inhibition parameter in the absence of Ag (I) (B) mol dm^{-3}**	**Inhibition parameter in the presence of Ag (I) (B) mol dm^{-3}**
Sodium benzoate	3.68 x 10^{4}	1.48 x 10^{3}
Benzamide	4.78 x 10^{4}	1.91 x10^{3}

5. DISCUSSION

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 = 4.05-5.25 the following equilibrium operates.

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

In this range of pH both species HSO_3^{-1}, SO_3^{-2} are present but former one present predominantly. The order of reaction was 0.20 indicates that it is almost independent of pH which is co-relate with the work of Irena – Wilkkosz *et al.* (2008) [31]. Gupta *et al.*(2008, 2011-2012) [32-34], Sharma *et al.* who studied the inhibiting effect of isoamyl alcohol, (2015)[35] formic acid, (2015)[36] isopropyl alcohol,(2016)[37], aniline (2017)[38], benzamide (2017) [39]sodium benzoate (2017) [40] in the presence of Ag (I) catalysed autoxidation of $SO_2$and reported the they all are influence the SO_2oxidation in atmosphere with different rate.The rate of uncatalysed and Ag (I) catalysed reaction is decelerated by the addition of sodium benzoate and benzamide in the present study. Manoj *et al.* (2008)[41] Sameena *et al.* (2013)[42]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 benzoate and benzamide are found to be in the range. This is strongly support the radical mechanism in the present case too based on the observed results.

$$HSO_3^{-1} \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{-2} \quad K_d = 5.01 \times 10^{-7} \tag{13}$$

$$Ag^+ + {}^-O_2CCH_3 \overset{K_{oAc}}{\rightleftharpoons} AgO_2CCH_3 \quad K_{oAc} = 2.29 \tag{14}$$

$$Ag^+ + SO_3^{-2} \overset{K_1}{\rightleftharpoons} AgOSO_2^- \quad K_1 = 2.51 \times 10^5 \tag{15}$$

$$Ag^+ + HSO_3^{-1} \overset{k_2}{\rightleftharpoons} AgHSO_3 \tag{16}$$

$$AgOSO_2^- + O_2 \overset{K_3}{\rightleftharpoons} AgOSO_2^{-1}.O_2 \tag{17}$$

$$AgHSO_3 + O_2 \overset{K_4}{\rightleftharpoons} AgHSO_3.O_2 \tag{18}$$

$$AgHSO_3.O_2 \xrightarrow{k_1} Ag^+ + HSO_5^- \tag{19}$$

$$HSO_5^- + HSO_3^{-1} \xrightarrow{k_2} \overset{-\bullet}{SO_4} + \overset{-\bullet}{SO_3} + H_2O \tag{20}$$

$$AgOSO_2^{-1}.O_2 \xrightarrow{k_3} Ag^+ + \overset{-\bullet}{SO_3} + O_2 \tag{21}$$

$$\overset{-\bullet}{SO_3} + O_2 \xrightarrow{k_4} \overset{-\bullet}{SO_5} \tag{22}$$

$$\overset{-\bullet}{SO_5} + SO_3^{-2} \xrightarrow{k_5} \overset{-\bullet}{SO_3} + SO_5^{-2} \tag{23}$$

$$\overset{-\bullet}{SO_5} + SO_3^{-2} \xrightarrow{k_6} SO_4 + SO_4^{-2} \tag{24}$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_7} 2SO_4^{-2} + SO_4^{-2} \tag{25}$$

$$\overset{-\bullet}{SO_4} + SO_3^{-2} \xrightarrow{k_8} SO_3 + SO_4^{-2} \tag{26}$$

$$\overset{-\bullet}{SO_4} + x \xrightarrow{k_9} \text{Non Chain product} \tag{27}$$

$$\overset{-\bullet}{SO_4} + \text{organics} \xrightarrow{k_{10}} \text{Non Chain product .} \tag{28}$$

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

$$k_1[Ag(I)(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{organics}]\}\,[SO_4^{-1}]. \tag{29}$$

Since the reaction is completely stopped in the presence of [Organics] = 2×10^{-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 organics by omission and substitution from the above mechanism the following rate law can be obtain (30)

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

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} and 1.91×10^4 mol dm^{-3} by sodium benzoate and benzamide respectively 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 SO_2 by formic acid is 3.58×10^3 mol dm^{-3} (Table- 4)So on the basis of calculated value of *B* we concluded that organics act as an free radical scavenger in silver (I) catalysed autoxidation of aqueous SO_2 in acidic medium and a free radical mechanism can operate in this system.

6. CONCLUSIONS

- The role of organics act as an inhibitor in silver (I) catalysed autoxidation of SO_2 in acidic medium has been find, and based on the observed results rate law a free radical mechanism has been proposed.

$$-d\,[(SIV)/dt \;=\; (k_1 + k_2[Ag])\,[(SIV)]/\,1 + B\,[organics]$$

$$R_{cat} = k_1\,[Ag(I)]\,[S(IV)]\,/\;\{k_9[x] + k_{10}[organics]\}\,.$$

- Based on the experimental results, rate constants and order of the reactions were determined. The reaction order in SO_2 was pseudo- first order for both reactions in the presence and absence of organics.
- The effect of pH on SO_2 oxidation in the presence of silver (I) and organics has been studied and found rate of the SO_2 oxidation depends on the initial pH of the solution but it is independent of the pH change during the reaction.
- The effects of temperature of solution on SO2 oxidation catalysed by silver (I) in presence of organics were discussed. By plotting a graph between *log k* v/s *1/T* yield gives us an apparent empirical energy of activation which is found33.12 kJ mol^{-1} for sodium benzoate and 40.56 kJ $mol^{-1}$for benzamide respectively.
- The value of inhibition factor *(B)* of both uncatalysed and silver (I) catalysed autoxidation of SO_2 in the presence of sodium benzoate and benzamide study here found $1.48x10^4$mol dm^{-3} and $1.91x10^4$mol dm^{-3} which is confirm that benzamide is best inhibitor compare to sodium benzoate which is also coincide by E_a lower for sodium benzoate compare to benzamide.

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8. REFERENCES

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