Co_2O_3 Catalysed and Uncatalysed autoxidation of S (IV) and its inhibition by different organics in alkaline Medium

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Abstract: In this paper we report that acetic acid and oxalic acid are good inhibitor for SO_2 oxidation in pH range 7.80- 9.40 in the presence of Co_2O_3. Based on the observed results following rate law given and a free radical mechanism has been proposed.

$$d[S(lV)]/dt = (k_1 + k_2[Co_2O_3]) [S(lV)]/1 + B [Organics]$$

Experiments were carried out at $30 \leq T°C \leq 40$, $7.80 \leq pH \leq 9.40$, 1×10^{-3} mol/cm$^3 \leq [S(lV) \leq 6 \times 10^{-3}$ mol/cm^3, 0.1gm dm$^3 \leq [Co_2O_3] \leq 0.5$gdm^3, 1×10^{-7} mol/cm$^3 \leq [organics] \leq 2 \times 10^{-4}$ mol/cm^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.

Keywords: Kinetics; Autoxidation; SO_2; Co_2O_3; Catalysis; Inhibition ; organics {acetic acid , oxalic acid}

INTRODUCTION:-

The atmospheric reactions of SO_2 and NO_x etc. are major acid rain precursors and are responsible for acidification of various forms of atmospheric water [1]. Studies of our country, the level of SO_2 in atmospheric environment is increasing gradually and therefore the danger of acid rain cannot be simply under estimated [2]. Studies in India and abroad have shown that anthropogenic sources in the atmosphere are the major contributors of SO_2 and NO_x which are transformed in to acids such as HNO_2, HNO_3, H_2SO_3 and H_2SO_4.

The catalytic role of several metal oxides such as CoO[3]; Co_2O_3[4]; Ni_2O_3[5]; CuO[6]; MnO_2[7]; and Cu_2O[8] in acidic medium has been reported. The S (IV) autoxidation reaction is known to proceed via both radical and non-radical mechanisms (Gupta et al) [9].

An interesting feature of many radical reactions is that, the reaction rate is inhibited by organics such as acetic acid, oxalic acid(Irena Wilkoszet al) [10], alcohols (Ziajkaet al) [11], carboxylic acid (Bostjan podkrojsek et al) [12], and ammonia(Gupta el al) [13], formic acid, isopropyl alcohol, isoamyl alcohol, aniline, benzamide, sodium benzoate (Sharma et al) [14-19].

In Indian sub-continent, the pH of the rain water lies in the range 6.5-8.5. Recently the influence of some low weight mono (formic, acetic) and di-carboxylic acids (oxalic, malic, malonic) on the Mn(II)-catalysed S(IV) oxidation has also been investigated[20-21].

This necessitates the study of autoxidation of sulfur (IV) in alkaline medium. In most of the studies the role of organics has been reported in the metal ion catalysed autoxidation of sulfur(IV) in aqueous medium [22-23]. Since in this paper we present the comparison of oxalic acid and acetic acid to know better inhibitor for SO_2 oxidation in alkaline medium in Co_2O_3 catalysed reaction. But still combined effect of organic compounds like alcohols and 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 Co_2O_3 catalysed oxidation of S(IV) by O_2 in alkaline medium in the presence of two organics i.e. oxalic acid and acetic acid to examine their effect on the reaction rate.

EXPERIMENTAL

The experimental procedure was exactly the equivalent to described earlier by Prasad et al [24]. All chemicals substances utilized were of reagent grade and their solution were ready in double distill water. The reactions were directed in 0.15-L Erlenmeyer flasks, open to air and to permit the part of atmospheric oxygen. The flask was placed in a beaker, which had a inlet at the lower part and an outlet at the upper part for circulating thermostatic water for keeping up with the desired temperature, $30\pm0.1°C$. The reaction were started by adding the desired volume of standard Na_2SO_3 solution for the reaction combination containing different added substances like buffer and catalyst oxide. The reaction mixture was stirred continuously and magnetically at 1600 ± 100 rpm to

permit the part of atmospheric oxygen and to save the reaction from becoming oxygen mass exchange controlled. The kinetics were concentrated in buffered medium, in which the pH remained fixed all through the whole course of reaction. For this reason, 10 cm^3 of buffer medium from Na_2HPO_4 (0.08 mol dm^{-3}) and KH_2PO_4 (0.02 mol dm^{-3}) for basic alkaline medium were used (complete volume 100 cm^3) for getting the desired pH.

The kinetic were followed by withdrawing the aliquot examples periodically and titrating the unreacted S(IV) iodometrically in slightly acidic medium as described earlier. The reproducibility of the replicate measurements was generally better than compared to ± 10%. All calculations were performed in MS Excel.

PRODUCT ANALYSIS-

When the reaction was complete, Co_2O_3 was filtered out and sulphate was estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure [25].

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

$$S(IV) + 0.5 O_2 \longrightarrow S(IV) \qquad (1)$$
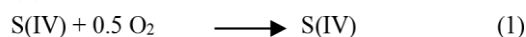
Results: Preliminary Investigation—

The kinetics of both uncatalysed and Co_2O_3 Catalysed reaction were studied in alkaline medium in pH 7.80-9.40 and temperature 30°C. In both of 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 1 From the fig 1 it is observed that both the uncatalysed and Co_2O_3 catalysed autoxidation of S (IV) reaction are inhibited by oxalic acid and acetic acid respectively.
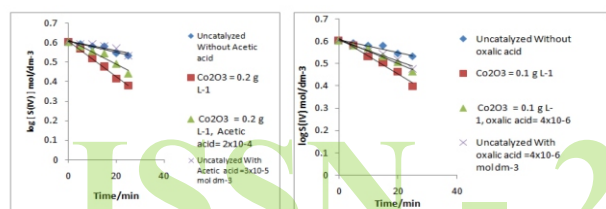

Fig.1 The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2x10^{-3} mol dm^{-3} at pH = 7.80, t = 30 °C

Uncatalysed Reaction

In this study the reaction was studied without adding Co_2O_3. As it is well known that the uncatalysed reaction is started by the trace metal particle impurities present in the reagent samples and distilled water utilized for the preparation of solution.

Dependence of S (IV)

The detailed dependence of the reaction rate on [S(IV)] was studied by varying sulphite is the range of 1×10^{-3} mol dm^{-3} to 6×10^{-3} mol dm^{-3} at pH= 7.80, t = 30°C in phosphate buffer medium. The kinetic was found to be first order in [S(IV)] as shown in Fig 1 and log [S(IV)] versus time plots were linear. The values of first order rate constant, k_1 are shown in table -1. The dependence of reaction rate on [S(IV)] follows the following 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)] at pH = 7.80, t = 30 ^{o}C CH_3COONa =8x10^{-2} mol L^{-1} CH_3COOH=2x10^{-2} mol L^{-1}

[S(IV)] mol dm^{-3}	0.001	0.002	0.003	0.004
(10^4) k_1 s^{-1}	1.06	1.07	1.01	1.05

[Organics] Dependence

The major aim of this study was to examine the effect of oxalic acid and acetic acid which are known as organics on the autoxidation of S(IV) in buffer medium and varying the [Organics] from 1x10^{-7} mol dm^{-3} to 2x10^{-4} mol dm^{-3} we observed the rate of the reaction decreased by increasing [Organics] The results are given in Table 2.

The nature of the [S(IV)] dependence in presence of organics did not change and remains first order. The first order rate constant k_{inh}, in the presence of organics was defined by rate law (3)

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

The values of k_{inh} at different [organics] are given in table 2 **Table 2** The values of k_{inh} at different [Organics] at pH = 7.80, t = 30 ^{o}C CH_3COONa = 8x10^{-2} molL^{-1} CH_3COOH= 2x10^{-2} mol L^{-1}.

[acetic acid] mol dm^{-3}	10^4 k_{AA} s^{-1}	1/k_{AA} s	[oxalic acid] mol dm^{-3}	10^4 k_{OA} s^{-1}	1/k_{OA} s
1.0x10^{-7}	3.82	2617	1.0x10^{-7}	3.65	2740
3.0x10^{-7}	3.19	3134	3.0x10^{-7}	3.12	3205
2.0x10^{-6}	2.60	3846	2.0x10^{-6}	2.10	4761
5.0x10^{-6}	2.21	4524	5.0x10^{-6}	1.80	5556
1.0x10^{-5}	1.02	803	8.0x10^{-6}	1.39	7194
3.0x10^{-5}	0.94	10638	1.0x10^{-5}	0.47	21276
			3.0x10^{-5}	0.31	32258

The valuve of first order rate constant k_{inh} in the presence of organics decreased with increasing [organics] in agreement with the rate law.

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

Where B is inhibition parameter for rate inhibition by organics

The equation (4) on rearrangement becomes

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

In accordance with the equation (5) the plot of 1/k_{inh} v/s [oxalic acid] and [acetic acid] was found to be

linear with positive intercept . The values of intercept $(1/k_1)$ and slope (B/k_1) were found to be 1.7×10^3 mol dm^{-3}s and 1.33×10^5 and 3.6×10^3 s and 2.68×10^7 mol dm^{-3}s at pH = 7.80, t = 30 °C respectively. From these values the value of inhibition parameter B was found to be 7.51×10^3 mol dm^{-3} and 7.36×10^3 mol dm^{-3} respectively
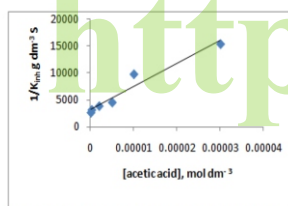

Fig. 2 Effect of acetic acid at [S(IV)] = 2×10^{-3} mol dm^{-3}, pH=7.80 and temp = 30°C, in phosphate buffered medium
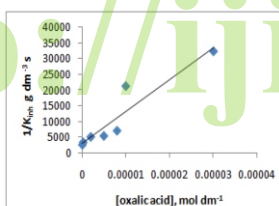
Fig.3 Effect of acetic acid at [S(IV)] = 2×10^{-3} mol dm^{-3}, pH=7.80 and temp = 30°C, in phosphate buffered medium

Co_2O_3 Catalysed Reaction

The kinetics of Co_2O_3 Catalysed autoxidation of S(IV) was studied in alkaline medium in the absence of inhibitor oxalic acid and acetic acid respectively.

[S(IV)] Variation

The dependence of S (IV) on reaction rate was studied by varying [S(IV)] from 1×10^{-3} mol dm^{-3} to 9×10^{-3} mol dm^{-3} at two different but fixed [Co_2O_3] of 0.1 and 0.2 g dm^{-3} at pH = 7.80, t = 30 ° The kinetics was found to be first order in [S(IV)] v/s time were linear as shown in Fig 1.

Co_2O_3 variations

The dependence of Co_2O_3 on the reaction rate was studied by varying Co_2O_3 from 0.1 and 0.2 g dm^{-3} at S(IV) = 2×10^{-3} mol dm^{-3} pH=7.80, t= 30 ° C in alkaline buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig 4. The nature of dependence of k_{cat} on Co_2O_3 was indicated as two term rate law (6)

$$-d\,[S(IV)]\,/dt = k_{cat}\,[S(IV)] = (k_1 + k_2[Co_2O_3])\,[S(IV)] \quad (6)$$

$$Or\ k_{cat} = k_1 + k[Co_2O_3] \quad (7)$$

From the plot in fig 4 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be 3.9×10^3 s and 3.6×10^{-3} mol dm^{-3} respectively at pH = 7.80, t = 30 °C, in alkaline buffered medium.
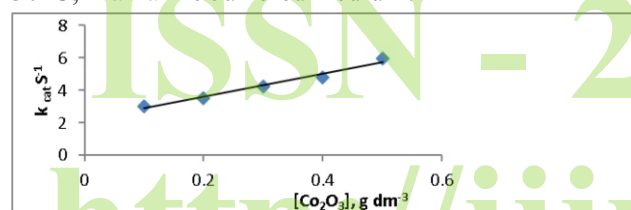
Fig.4 The dependence of catalyst concentration at [S(IV)] = 2×10^{-3} mol dm^{-3} pH = 7.80, t = 30 °C, in alkaline buffered medium.

Rate law in the Presence of organics

A detailed study of dependence of rate on S(IV), [Co_2O_3] and pH with in the presence of organics {oxalic acid and acetic acid} revealed that the kinetics remain first order both in S(IV) and [Co_2O_3] and independence of pH obeys the following rate law.

$$-d[S(IV)]\,/dt = (k_1 + k_2[Co_2O_3])\,[S(IV)]\,/1 + B\,(Organics) \quad (8)$$

$$Where\ k_{inh} = (k_1 + k_2[Co_2O_3])\,/1 + B\,(Organics) = k_{cat}\,/1 + B\,(Organics) \quad (9)$$

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

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

Table3 The values of k_{inh} at different [Organics] at [Co_2O_3]=0.1gm dm^{-3}, pH – 7.80, t – 30 °C CH$_3$COONa = 8×10^{-2} molL^{-1} CH$_3$COOH = 2×10^{-2} mol L^{-1}.

[acetic acid] mol dm^{-3}	10^4 k$_{OA}$ s^{-1}	1/k$_{OA}$ s	[oxalic acid] mol dm^{-3}	k$_{AA}$ s^{-1}	1/k$_{AA}$ s
1.0×10^{-7}	5.93	1686	1.0×10^{-7}	4.87	2053
2.0×10^{-7}	4.27	2341	2.0×10^{-7}	3.71	2695
4.0×10^{-7}	3.91	2557	4.0×10^{-7}	3.12	3205
6.0×10^{-7}	3.71	2695	6.0×10^{-7}	2.86	3496
2.0×10^{-6}	3.30	3030	2.0×10^{-6}	2.18	4587
4.0×10^{-6}	2.04	3289	4.0×10^{-6}	2.10	4761
8.0×10^{-6}	2.35	4255	8.0×10^{-6}	1.36	7352
1×10^{-5}	2.07	4830	1×10^{-5}	0.57	17543
5×10^{-4}	1.98	5050			
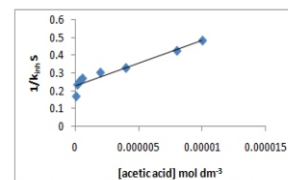
Fig 5 Plot of 1/k$_{inh}$ vs [acetic acid] at [S(IV)] = 2×10^{-4} mol dm^{-3}, temp = 30°C, [Co_2O_3]=0.1g, and pH = 7.80 in phosphate. buffered medium
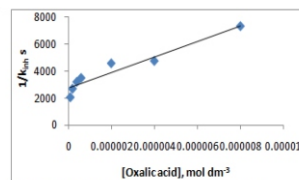
Fig 6 Plot of 1/k$_{inh}$ vs [oxalic acid] at [S(IV)] = 2×10^{-4} mol dm^{-3}, temp = 30°C, [Co_2O_3]=0.1g, and pH = 7.80 in phosphate buffered medium.

From Fig.5 & Fig.6 graph the value of $B_{A.A}$ and $B_{O.A}$ are found as 3.5×10^3 mol dm^{-3} and 5.78×10^3 mol dm^{-3} respectively.

Variation of pH

Variation of pH was carried out from 7.80-9.40 at different [S(IV)], Co_2O_3, [oxalic acid], [acetic acid] and temperatures. The rate decreases slightly by varying pH is inverse H$^+$ ion dependence was observed. From the plot of log k_1 v/s log (H$^+$). The effect of [buffer] was examined by varying the concentration of both Na_2HPO_4 & KH_2PO_4 so that the ratio [Na_2HPO_4]/[KH_2PO_4] remained same, so pH remained fixed. The values showed that the rate of reaction to be insensitive to the buffer concentration. The results are given table-3

Table-3 Effect of $_pH$ at [S(IV)] = 2×10^{-3} mol dm^{-3} at Co_2O_3 = 0.2 g dm^{-3} [acetic acid]= 2.0×10^{-4} mol dm^{-3} [oxalic acid]= 4.0×10^{-6} mol dm^{-3}

pH	7.80	8.50	8.90	9.40
10^4 k$_{A.A}$ s^{-1}	2.31	2.92	2.86	2.92
10^4 k$_{O.A}$ s^{-1}	2.27	2.73	2.52	2.44

Effect of temperature

The values of k_{obs} were determined at different temperatures in the range of 30°C to 40°C. The results are given in Table 4. By plotting a graph between log k v/s 1/t yield us an apparent empirical energy of activation 89.57 kJ mol^{-1} and 87.40 kJ mol^{-1} in the
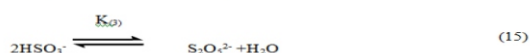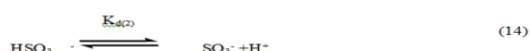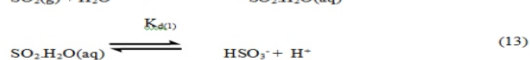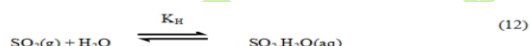
presence of oxalic acid and acetic acid respectively.

Table 4 Effect of temperature at [S(IV)] = 2×10^{-3} mol dm^{-3} at Co$_2$O$_3$= 0.2 g dm^{-3} [oxalic acid]= 4×10^{-6} mol dm^{-3} [acetic acid]= 2.0×10^{-4} mol dm^{-3} pH =7.80 .

t ºC	30⁰C	35 ºC	40ºC
$10^4 k_{O.A.S}^{-1}$	2.27	5.21	7.05
$10^4 k_{A.A.S}^{-1}$	2.31	5.19	6.98

5. DISCUSSION:

In aqueous solution SO$_2$ is present in four forms SO$_2$.H$_2$O, HSO$_3^{-1}$, SO$_3^{-2}$, S$_2$O$_3^{-2}$ governed by the following equations.

$$SO_2(g) + H_2O \underset{}{\overset{K_H}{\rightleftharpoons}} SO_2.H_2O(aq) \tag{12}$$

$$SO_2.H_2O(aq) \overset{K_{s(1)}}{\rightleftharpoons} HSO_3^- + H^+ \tag{13}$$

$$HSO_3^- \overset{K_{s(2)}}{\rightleftharpoons} SO_3^- + H^+ \tag{14}$$

$$2HSO_3^- \overset{K_{(3)}}{\rightleftharpoons} S_2O_5^{2-} + H_2O \tag{15}$$

In this experimental study in pH range (7.80 - 9.40), S(IV) would be generally present as SO$_3^{2.}$ Since the rate of reaction of under study not depends on pH, we have considered only SO$_3^2$ species to be reactive.

In a several transition metal oxide catalysed heterogeneous aqueous phase autoxidation reactions of sulfur(IV), the development of surficial complexes by adsorption of sulfur(IV) and O$_2$ on the molecule surface and oxidation of sulfur (IV) occur through the intervention of different oxidation states has been proposed. In the present study, the dependence of oxygen shows that the formation of surficial complex by adsorption of O$_2$ and So$_3^{-2}$ on the molecule surface of Co$_2$O$_3$ through the fast steps.

$$Co_2O_3 + SO_3^{2-} \overset{K_1}{\rightleftharpoons} Co_2O_3.\,SO_3^{2-} \tag{16}$$

$$Co_2O_3.SO_3^{2-} + O_2 \overset{K_2}{\rightleftharpoons} Co_2O_3.SO_3^{2-}.\,O_2 \tag{17}$$

$$Co_2O_3.\,SO_3^{2-}.O_2 \overset{k_1}{\rightarrow} Co_2O_3 + SO_3^{\overrightarrow{\cdot}} + O_2^{\cdot} \tag{18}$$

$$SO_3^{\overrightarrow{\cdot}} + O_2 \overset{k_2}{\rightarrow} SO_5^{\overrightarrow{\cdot}} \tag{19}$$

$$SO_5^{\overrightarrow{\cdot}} + SO_3^{2-} \overset{k_3}{\rightarrow} SO_5^{2-} + SO_3^{\overrightarrow{\cdot}} \tag{20}$$

$$SO_5^{\overrightarrow{\cdot}} + SO_3^{2-} \overset{k_4}{\rightarrow} SO_4^{\overrightarrow{\cdot}} + SO_4^{2-} \tag{21}$$

$$SO_5^{2-} + SO_3^{2-} \overset{k_5}{\rightarrow} 2SO_4^{2-} \tag{22}$$

$$SO_4^{\overrightarrow{\cdot}} + SO_3^{2-} \overset{k_6}{\rightarrow} SO_4^{2-} + SO_3^{\overrightarrow{\cdot}} \tag{23}$$

$$SO_4^{\overrightarrow{\cdot}} + x \overset{k_7}{\rightarrow} \text{Non chain product} \tag{24}$$

$$SO_4^{\overrightarrow{\cdot}} + \text{organics} \overset{k_8}{\rightarrow} \text{Non chain product} \tag{25}$$
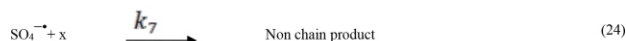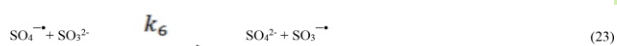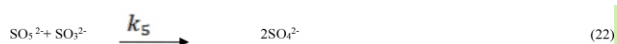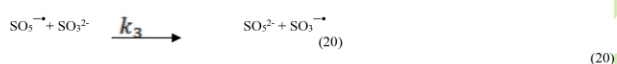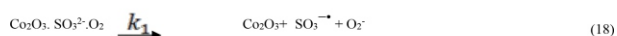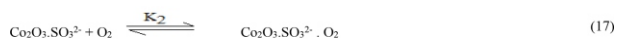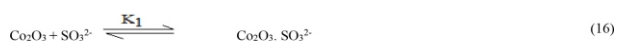
In alkaline medium the rate of Co$_2$O$_3$ catalysed reaction is highly decelerated by the addition of organics acetic acid and oxalic acid like that of reported by Husain et al [26-29] and like that of ethanol reported by Gupta et al [30] respectively. this shows the operation of a radical mechanism including oxy sulfur free radicals, as SO$_3$–, SO$_4$–and SO$_5$–. The inhibition is caused through the scavenging of SO$_4$–by inhibitors such as ethanol and benzene etc.

A reported by Sameena et al [31] a radical mechanism operates in those reaction in which the inhibition parameter lies the reach 10^3-10^4. In this investigation the value of the inhibitor parameter is found to be 7.3×10^3 and 7.5×10^3 in the presence of acetic acid and oxalic acid respectively, which lies in the same range. This strongly supports the radical mechanism for the Co$_2$O$_3$ – catalysed reaction in presence of organics. Based on the observed result including the inhibition by organics, the above radical mechanism is proposed which like that proposed by Prasad et al [32], Mudgal et al [33] in the oxalic acid and ethanol inhibition of the Co$_2$O$_3$ catalysed reaction respectively.

In the mechanism, no role is assigned to O$_2^{-}$, which is additionally known to react with sulfur (IV) slowly. It might disproportionate to form H$_2$O$_2$ and O$_2$ or may be scavenged by contaminations. In the present study the value of inhibition parameter for uncatalysed and Co$_2$O$_3$ catalysed autoxidation of S (IV) by acetic acid and oxalic acid are found to be in the range. This is strongly support the radical mechanism in the present case too based on the observed results.

By assuming long chain hypothesis and steady state approximation d[SO$_3^-$]/dt, d[SO$_4^-$]/dt and d[SO$_5^-$]/dt to zero it can be shown that the rate of initiation is equivalent to the rate of termination.eq. 26

$$k_1[Co_2O_3(SO_3^{2-})(O_2)]=\{k_7[X]+k_8[\text{organics}]\}[SO_4^-] \tag{26}$$

Since the reaction is completely stopped with the presence of [acetic acid] at 1×10^{-3} mol dm^{-3} and [oxalic acid] 1×10^{-5} mol dm^{-3} at so the steps (18) and (22) appear to be insignificant. The contribution of propagation reaction (21) has been signification in the Co$_2$O$_3$ catalysed. Reaction where the autoxidation

reaction should have not take place in the presence of high organics concentration i.e. the reaction is completely seized in the presence of high concentration of organics . This drove us to the rate of reaction given by equation (27).

$$-d[S(IV)]/dt = R_{cat} = k_6 [SO_4^{-\bullet}] [SO_3^{2-}] \qquad (27)$$

By substituting the value of $(SO_4^{-\bullet})$ we get

$$R_{cat} = \frac{k_6 k_1 [Co_2O_3. SO_3^{2-}, O_2] [SO_3^{2-}]}{k_7[x] + k_8 [organics]} \qquad (28)$$

From equilibria 16 & 17

$$R_{cat} = \frac{k_6 k_2 k_1 [Co_2O_3] [S(IV)] [O_2]}{\{1 + k_1[S(IV)]\} \{k_7 [x] + k_8 [organics]\}} \qquad (29)$$

At fixed O_2, replacing $k_6 k_1 k_2[O_2]$ by k^1 we get

$$R_{cat} = \frac{k^1 [Co_2O_3] [S(IV)]}{\{1[S(IV)]\} \{k_7 [x] + k_8 [organics]\}} \qquad (30)$$

Since we observe a first order in [S(IV)], the value of $K_1 [S(IV)] \ll 1$ so the above rate law can be reduce to.

$$R_{cat} = \frac{k^1 [Co_2O_3] [SO_3^{2-}]}{K_7[x] + k_8 [organics]} \qquad (31)$$

Or $R_{cat} = k^1 [Co_2O_3] [SO_3^{2-}] / K_7[x] + k_8 [organics]$

Sharma et al [34-36] proposed a similar mechanism for the Ag(I) catalysed autoxidation of sulfur dioxide inhibition by organics, which lead to a similar rate law. By comparing derived rate law and the experimental rate law we observe the similarity in these two. The calculated value of inhibition constant B is 3.5×10^3 mol^{-1} dm^3 and 5.7×10^3 mol^{-1} dm^3 by acetic acid and oxalic acid respectively . which is in the range of 10^3 to 10^4. So on the basis of the calculated value of B, we concluded that organics act as a free radical scavenger in the Co_2O_3 catalysed autoxidation of aqueous sulfur dioxide in a alkaline medium and a free radical mechanism can operate in this system.

Conclusion-

The following conclusions are deduced from the results of the organics {oxalic acid and acetic acid} inhibited Co_2O_3 catalysed autoxidation of S(IV) was that inhibit the oxidation with the fast influence. The value of Inhibition factor of both uncatalysed and Co_2O_3 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. The value of inhibition factor (B) of both uncatalysed and Co_2O_3 catalysed autoxidation of SO_2 in the presence of acetic

acid and oxalic acid study here found 3.5×10^3 mol dm^{-3} and 5.78×10^3 mol dm^{-3} which is confirm that oxalic acid is best inhibitor compare to acetic acid which is also coincide by E_a higher for oxalic acid compare to acetic acid.

Environmental Importance –

Organics are competent 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. The results 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 S(IV) by O_2

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