Original Article

Bulletin of Pure and Applied Sciences.
Vol.39 C (Chemistry), No.1, 2020: P.38-49
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2020.00005.9

http://www.bpasjournals.com/chemistry

Role of Iso Amyl Alcohol (IAA) on CO_2O_3 Catalysed Autoxidation of SO_2 in Atmospheric Water

Abstract

The kinetics of the iso amyl alcohol inhibited CO_2O_3 catalysed autoxidation of sulfur (IV) in alkaline medium has been studied and based on the observed results rate law and a free radical mechanism has been proposed.

Keywords: Kinetics; Autoxidation; SO_2; CO_2O_3; Catalysis; Inhibition; IAA.

S. Begam[1]
F. Hussain[2]
D.S.N. Prasad[3]*

Author Affiliations
[1,2,3]Department of Chemistry
Govt. P. G. College, Jhalawar, Rajasthan 326001, India

***Corresponding Author**
D.S.N. Prasad,
Associate Professor, Department of Chemistry
Govt. P. G. College, Jhalawar, Rajasthan 326001, India

E- mail: dsnp308@gmail.com

Received on 28.01.2020
Accepted on 27.04.2020

1. INTRODUCTION

A large number of studies have been done on the atmospheric oxidation of sulfur (IV) in the recent past, in aerosols and in bulk aqueous phase. The trace metal ions which are part of all atmospheric systems and are catalyzing the oxidation of aqueous sulfur dioxide in to acid sulfate [1]. The reviews by Huie and peterson, Hoffmann and Boyce, Hoffmann and Jacob deal with the oxidation of sulfur (IV) by transition metal ions and their role in catalyzing the dioxygen-S (IV) systems [2]. The metal oxides, which are released to the atmosphere as a result of combustion processes are integral part of suspended particulate matter [3]. The catalytic role of several metal oxides such as CoO [4], CO_2O_3 [5], Ni_2O_3 [6], CuO [7], MnO_2 [8] and Cu_2O [9] and MnO_2 [10] in acidic medium has been studied and given a two term rate law. Gupta et al studied the inhibiting effect of alcohol on the CoO, Co_2O_3 and Ni_2O_3catalysed autoxidation reaction in alkaline medium and proposed a radical mechanism for CoO and CO_2O_3 [11]. Biglow (1898) was first to report that, alcohols slow down the reaction between sodium sulphite and oxygen. Aleya and Back strom studied the inhibiting effect of aliphatic alcohols such as ethanol, iso propanol, secondary butanol and benzyl alcohol on the oxidation of sodium sulphite in alkaline conditions. Bostjan Podkrajsek *et al.* (2006) studied the effect of carboxylic acids on catalytic oxidation of sulfur(IV) and observed that mono-carboxylic acids inhibit the oxidation, formic acid shows strongest influence. Inhibition by glycolic,lactic and acetic acid is stronger at pH 4.5 than at 3.5.The most probable reason is the interaction between sulfate radicals and carboxylic acids. Connick and Zhang reported that the inhibition effect of methanol on autoxidation of sulfur (IV) in the presence of Mn(II) ions is complex and in which sulfate radicals are scavenged. An interesting feature of many radical reactions is that, the reaction rate is inhibited by organics [12-20] So far inhibiting effect of iso amyl alcohol on the metal oxide catalysed autoxidation of aqueous sulfur dioxide is not studied. So in view of the knowing the inhibiting effect of iso amyl alcohol on the Co_2O_3catalysed autoxidation of sulfur dioxide in the alkaline medium the present study is under taken.

2. EXPERIMENTAL

The experimental procedure was exactly the same as described earlier [21-25].

3. PRODUCT ANALYSIS

The product analysis showed the recovery of sulfate to be 98 ± 2% in all cases in agreement with Eq.1.

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

4. RESULTS

Preliminary Investigation

The kinetics of uncatalysed and Co_2O_3catalysed autoxidation reaction of S(IV) were studied in alkaline medium in the pH range 7.40-8.80 at t=30°C. In both the cases first order dependence in [S(IV)] was found and the treatment of kinetic data is based on the determination of first order rate constant k_1, from the plot of log [S(IV)] versus time, t plotsare shown in the Fig. 1

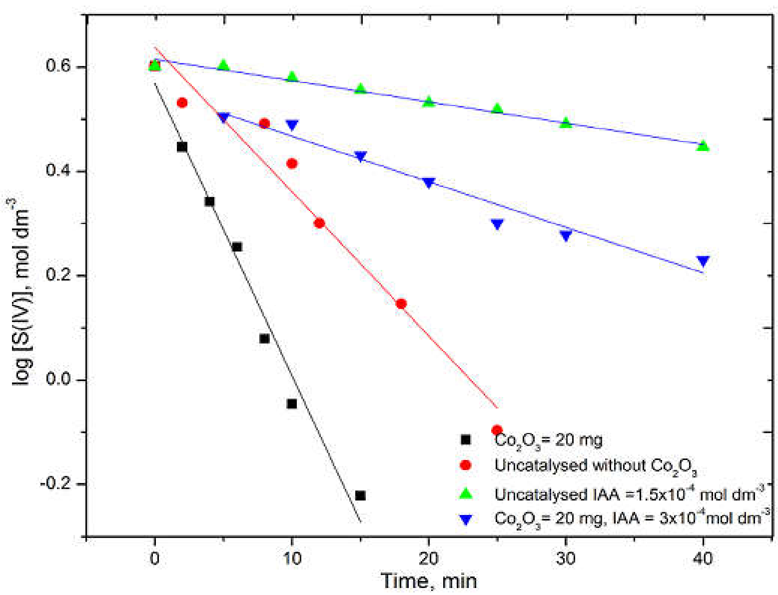

Figure 1: The disappearance of [S (IV)] with time in air - saturated suspensions of 100 ml at [S (IV)] = 2×10^{-3}mol L^{-1},at 30° C and pH = 7.40

Uncatalysed Reaction

In this study the reaction was studied without adding CO_2O_3 [26]

[S (IV)] Dependence

The dependence of [S (IV)] on the reaction rate was studied by varying from 1×10^{-3} mol L^{-1} to 6×10^{-3} mol L^{-1} at pH= 7.40 and t = 30°C in phosphate buffer medium. The kinetics was found to be first order in [S (IV)] and log [S (IV)] vs. time plots were linear. The results are given in table 1. The value of first order rate constant, k_1 are shown in table 1. The dependence of reaction rate on [S (IV)] follows the following rate low.

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

Table 1: The values of k_1 for Uncatalysed reactionat different [S (IV)] at pH= 7.40 and t = 30⁰C

[S(IV)]mol L^{-1}	$10^4 k_1$ s^{-1}
0.001	6.15
0.002	6.19
0.004	6.32
0.006	6.11

Iso amyl alcohol] dependence

The major aim of the present study was to examine the effect of organic inhibitors on the autoxidation of S (IV) in alkaline medium so for this purpose iso amyl alcohol was chosen as inhibitor. On varying the [iso amyl alcohol] from $.5\times10^{-3}$ to 4×10^{-3}mol L^{-1}, the rate of the reaction become decelerated. The results are given in table 2.The nature of the [S (IV)] – dependence in presence of iso amyl alcohol did not change and remained first order. The first order rate constant k_{inh} in the presence of iso amyl alcohol were defined by the following rate law (3)

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

The values of k_{inh}at different [iso amyl alcohol] are given in table 2

Table 2: The value of k_{inh}at [S (IV)] = 2 x 10^{-3} mol L^{-1}, pH= 7.40, t = 30°C

[I.A.A.]	k_{inh}	$1/k_{inh}$
0	6.19×10^{-4}	1616
0.5×10^{-3}	2.01×10^{-4}	2083
1.0×10^{-3}	1.31×10^{-4}	3703
2.0×10^{-3}	$.81\times10^{-4}$	4761
4.0×10^{-3}	$.534\times10^{-4}$	5263

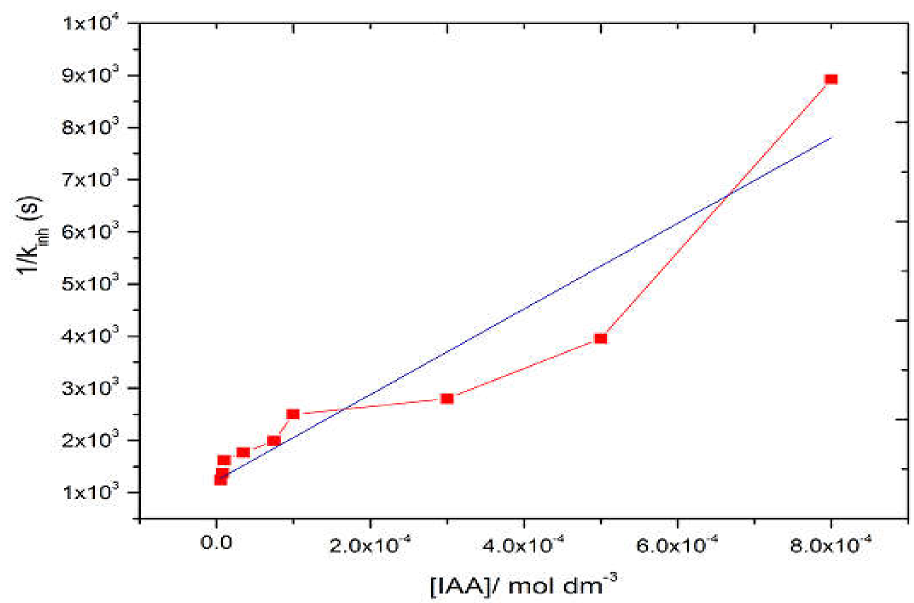

Figure 2: Effect of I.A.A. at [S (IV)] = 2 × 10^{-3}mol L^{-1}, pH = 7.40 and at 30°C, in phosphate buffered medium

The values of first order rate constant k_{inh} in the presence of iso amyl alcohol decreased, with increasing iso amyl alcohol in agreement with the rate law.

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

where B is inhibition parameter for rate inhibition by iso amyl alcohol.

By rearranging the equation (4) we get
$1/ k_{inh} = 1/ k_1 + B [IAA] / k_1$ (5)

In accordance with eq.(5) the plot of $1/ k_{inh}$versus [iso amyl alcohol] was found to be linear with a non-zero intercept, fig. 2 Where intercept $=1/k_1$ and slope $=B/k_1$ .The values of $1/ k_1$ and B/ k_1 were found to be **2.79×10^3 s** and **3.83×10^6 mol^{-1}L** at pH = 7.40, and t=30ºC. The value of slope/intercept gives us the value of inhibition parameter B, which was found to be **1.37×10^3 mol^{-1} L**.

CO_2O_3 -Catalyzed Reaction
The kinetics of CO_2O_3-catalysed autoxidation of S (IV) was studied in alkaline medium in the absence of inhibitor iso amyl alcohol.

[S (IV)] Variation
The dependence of reaction rate on [S (IV)] was studied by varying [S (IV)] from 1×10^{-3} to 10×10^{-3} mol L^{-1} at two different but fixed [CO_2O_3] of 0.1 and 0.2 g L^{-1} at pH = 7.40 and t=30°C. The kinetics was found to be first order in [S (IV)] as shown in Fig 6.1 and log [S (IV)] versus time plots were linear.

[CO_2O_3] Variation
The dependence of reaction rate on [CO_2O_3] was studied by varying [CO_2O_3] from 0.1gL^{-1} - 0.4gL^{-1} at fixed [S(IV)] of2×10^{-3} mol L^{-1} at pH=7.40 and t=30°C in phosphate buffer medium. The values of first order rate constants $k_{cat,}$ for S (IV) - autoxidation was determined at different [CO_2O_3]are given in table 3.

Table 3: The value of k_{cat} at different [CO_2O_3] at pH = 7.40 and t = 30°C

CO_2O_3(g L^{-1})	**$10^3 k_{cat}$ s^{-1}**
0.1	8.8
0.2	13.7
0.3	16.9
0.4	21.8

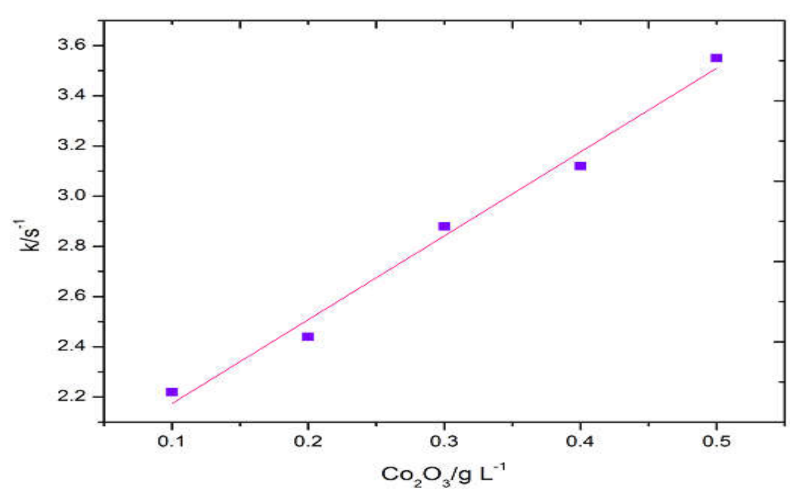

Figure 3: The dependence of rate on catalyst concentration at [S (IV)] = 2×10^{-3}mol L^{-1}, at t=30°C and pH = 7.40

The nature of dependence of k_{cat} on [CO_2O_3] shown in Fig 3 indicates the operation of a two term rate law

$-d[S (IV)]/dt = k_{cat} [S (IV)] = (k_1 + k_2 [CO_2O_3] [S (IV)]$ (6)
$K_{cat} = (k_1 + k_2 [CO_2O_3]$ (7)

from the plot in Fig 3. the values of intercept is equal to k_1 and slope is equal to k_2 were found to be **5.1 × 10^{-4} s** and **4.01 × 10^{-3} mol^{-1} L s,** respectively at pH= 7.40 and 30˚C.

Variation of pH

Variation in pH in the range 7.40 to 8.80 in phosphate buffer medium showed the rate to be independent of pH. The effect of [buffer] was examined by varying the concentration of both Na_2HPO_4& KH_2PO_4 in such a way that the ratio $[Na_2HPO_4]$ / $[KH_2PO_4]$ remained same, so that pH remained fixed. The values showed that the rate of the reaction to be insensitive to the buffer concentration in table 4

Table 4: Variation of pH at $[CO_2O_3]$ = 0.2 g L^{-1}, [I.A.A.] = .5×10^{-3}mol L^{-1} [S (IV) = 2×10^{-3}mol L^{-1} and t = 30°C

[S(IV)]molL^{-1}	$[CO_2O_3]$ g L^{-1}	[iso amyl alcohol] molL^{-1}	pH	temp.	10^4k_{cat} $k_1 + k_2[CO_2O_3]$
0.002	0.2	0.0005 M	7.40	30°C	5.85
0.002	0.2	0.0005 M	7.80	30°C	5.89
0.002	0.2	0.0005 M	8.10	30°C	5.88
0.002	0.2	0.0005 M	8.80	30°C	5.96

Variation of iso amyl alcohol

To know the effect of iso amyl alcohol on CO_2O_3- catalyzed autoxidation of S(IV), iso amyl alcohol variation was carried out from 0.5×10^{-3} to 6×10^{-3}mol L^{-1} at two different $[CO_2O_3]$ that is 0.1 and 0.2 g L^{-1} but fixed [S(IV)]= 2×10^{-3} mol L^{-1} at pH = 7.40 and t=30°C.The results indicates that by increasing the [iso amyl alcohol] the rate become decreases.

A detailed study was carried out for the dependence of rate on [S (IV)], $[CO_2O_3]$, and pH on the reaction in the presence of iso amyl alcohol revealed that the kinetics remain first order both in [S (IV)] and $[CO_2O_3]$ and independent of pH.

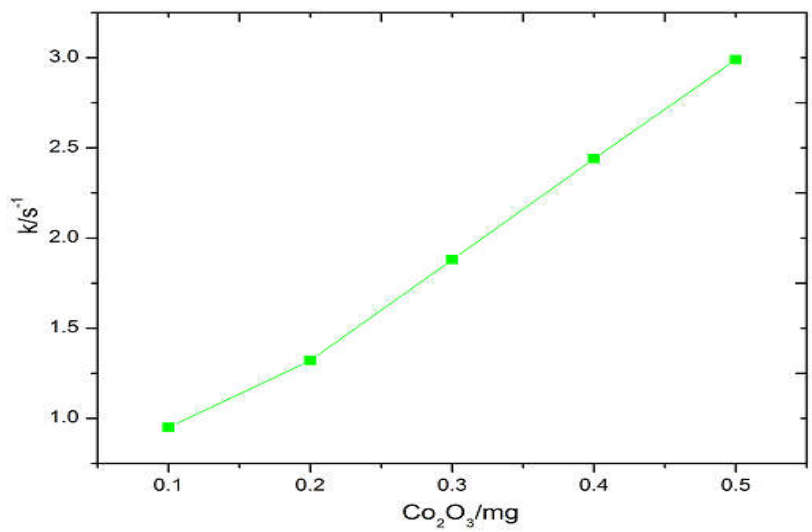

Figure 4: Effect of [S (IV)] at I.A.A. = 1.56×10^{-4} g L^{-1} , pH=7.40 and at 30°C, in phosphate buffered medium.

A plot between $[CO_2O_3]$ v/s first order rate constant is linear (fig. 4) with non-zero intercept. The value of intercept and slope are found to be **3.67× 10^{-5} s^{-1}** and **2.78 × 10^{-5} g^{-1} L s^{-1}** respectively. Depend upon the observed results the reaction follows the following rate law in the presence of iso amyl alcohol.

$-d[S(IV)]/dt = k_1 + k_2 [CO_2O_3] [S(IV)] / 1 + B [IAA]$ (8)

$K_{inh} = k_1 + k_2 (CO_2O_3]/1 + B[IAA] = k_{cat} /1 + B [IAA]$ (9)

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

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

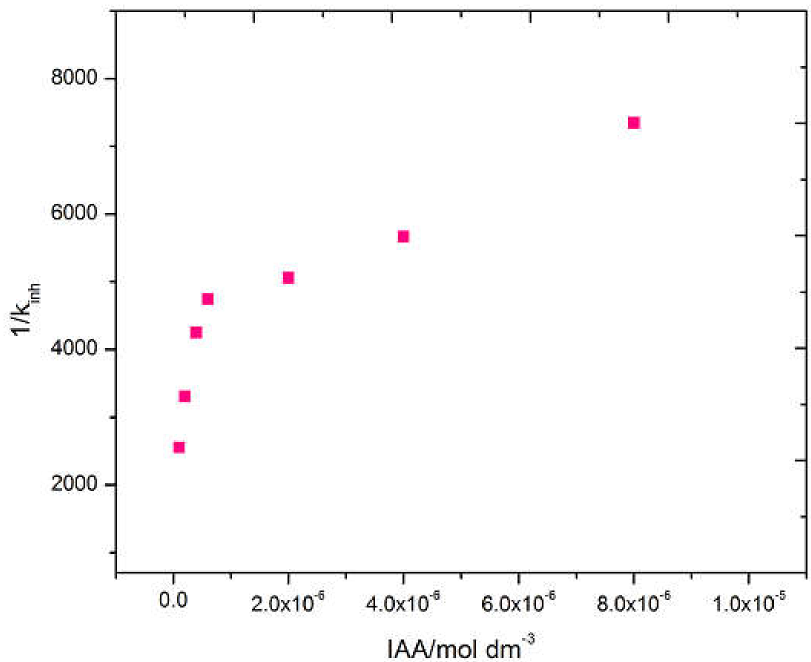

Figure 5: Effect of I.A.A. at [S (IV)] = 2 × 10^{-3}mol L^{-1} and at 30°C, CO_2O_3 = 10mg, in phosphate buffered medium.

By plotting a graph between $1/k_{inh}$ v/s [iso amyl alcohol] gives a linear line with non-zero intercept figure 5. The value of intercept = $1/k_{cat}$ and slope=B/k_{cat} from the graph these values are found to be **2.40 × 10^3 s** and **1.68× 10^6mol^{-1} L s** respectively.From these values the value of inhibition parameter B can be calculated, inhibition parameter B=slope/intercept that is B = **0.70 × 10^3 mol^{-1} L**.

Effect of temperature

To calculate the apparent empirical energy of activation the values of k_{obs} were determined at three different temperatures in the range 30**°C** to 40**°C.** The results are given in table 5 By plotting a graph between log k versus 1/t gives us the apparent energy of activation determined to be 24.18 kJ mol^{-1}.

Table 5: Effect of temperature on k_{obs} air saturated suspensions at [S(IV)] = 2 × 10^{-3}mol L^{-1}, [CO_2O_3] = 0.2 g L^{-1}, [I.A.A.] =.5×10^{-3}mol L^{-1},t = 30°C, and pH = 7.40.

t °C	10^4 k_{obs},s^{-1}
30	5.85
35	8.55
40	10.37

5. DISCUSSION

In aqueous solution SO_2 is present in four forms, $SO_2.H_2O$, HSO_3^-, SO_3^{2-} and $S_2O_5^{2-}$, governed by the following equations [27-30].

$$SO_2 + H_2O \overset{K_H}{\rightarrow} SO_2H_2O\,(aq.) \qquad (12)$$

$$SO_2H_2O\,(aq.) \overset{K_1}{\rightarrow} HSO_3^- + H^+ \qquad (13)$$

$$HSO_3^- \overset{K_2}{\rightarrow} SO_3^- + H^+ \qquad (14)$$

$$2HSO_3^- \overset{K_3}{\rightarrow} S_2\,O_5^{-2} + H_2\,O \qquad (15)$$

K_H is Henry"s constant and K_1, K_2 are acid dissociation constants. K_3 is the formation constant for $S_2O_5^{2-}$ at 25°C the values are K_H = 1.23 mol $L^{-1}atm^{-1}$, K_1=1.4×10^{-2}, K_2=6.24×10^{-8}, and K_3=7.6×10^{-2}. In this experimental study in pH range (7.40 – 8.80), S(IV) would be largely present as SO_3^{2-}. Since the rate of reaction is nearly independent of pH, we have considered only SO_3^{2-} species to be reactive in the subsequently. In the heterogeneous solid – liquid phase reaction of MnO_2 and S (IV), Halperin and Taube proposed that the sulfite ion makes bond through oxygen atom at the surface of solid MnO_2. In the present study, the dependence of oxygen shows that the formation of surficial complex by adsorption of O_2 on the particle surface of CO_2O_3 through the fast step. In alkaline medium the rate of CO_2O_3 catalysed reaction is highly decelerated by the addition of iso amyl alcohol like that of ethanol reported by Gupta et al [11] this indicates the operation of a radical mechanism involving oxysulfur free radicals, like $SO_3^{-\bullet}$, $SO_4^{-\bullet}$ and $SO_5^{-\bullet}$[31-32]. The inhibition is caused through the scavenging of $SO_4^{-\bullet}$ by inhibitors such as ethanol and benzene, etc. Podkrajsek *et al.* (2006) studied the effect of carboxylic acids on catalytic oxidation of sulfur (IV) and found that scavenging effect of formic acid is strongest. Inhibition of glycolic, lactic and acetic acid is stronger at pH 4.5 than at 3.5. The most probable reason is the interaction between sulfate radicals and carboxylic acids [33-34]. As reported by Gupta et al. a radical mechanism operates in those reactions in which the inhibition parameter lies the range 10^3-10^4. In this study the value of inhibitor parameter is found to be 0.70×10^3, which lies in the same range. This strongly supports the radical mechanism. For the CO_2O_3 – catalysed reaction in presence of iso amyl alcohol [35-36] Based on the observed results including the inhibition by iso amyl alcohol, the following radical mechanism is proposed which similar to that proposed by Gupta et al in the ethanol inhibition of the COO catalysed reaction [37].

$$CO_2O_3 + SO_3^{-2} \overset{K_1}{\rightarrow} CO_2O_3.SO_3^{-2} \qquad (16)$$

$$CO_2O_3.SO_3^{-2} + O_2 \overset{K_1}{\rightarrow} CO_2O_3.SO_3^{-2}.O_2 \qquad (17)$$

$$CO_2O_3.SO_3^{-2}.O_2 \overset{K_1}{\rightarrow} CO_2O_3 + SO_3^{-1} + O_2^{-1} \qquad (18)$$

$$SO_3^{-1} + O_2 \xrightarrow{k_2} SO_5 \quad (19)$$

$$SO_5 + SO_3^{-2} \xrightarrow{k_3} SO_3 + SO_5^{-2} \quad (20)$$

$$SO_5 + SO_3^{-2} \xrightarrow{k_4} SO_4 + SO_4^{-2} \quad (21)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_5} 2SO_4^{-2} + SO_4^{-2} \quad (22)$$

$$SO_4 + SO_3^{-2} \xrightarrow{k_6} SO_3 + SO_4^{-2} \quad (23)$$

$$SO_4 + x \xrightarrow{k_7} \text{Non Chain product} \quad (24)$$

$$SO_4 + IAA \xrightarrow{k_8} \text{Non Chain product} \quad (25)$$

In the mechanism, no role is assigned to O_2^- , which is also known to react with sulfur (IV) slowly. It may disproportionate to form H_2O_2 and O_2 or may be scavenged by impurities[20]. 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 equal to the rate of termination. Since the reaction is completely stopped in the presence of [I.A.A.] at 1.7×10^{-3}mol L^{-1}. so the steps (15) & (19) appear to be unimportant. The contribution of propagation reaction (18) been significant in the CO_2O_3 catalysed. Reaction where the autoxidation reaction should have occurred even in the presence of high iso amyl alcohol concentration. But this is not true and the reaction is completed seized in the presence of high concentration of iso amyl alcohol. This led us to ignore the step (18) and assume only the rate of reaction given by equation.

$$k_1[CO_2O_3(SO_3^{-2})(O_2)] = \{k_7[x] + k_8[IAA]\}[SO_4^{-1}] \quad (26)$$

$$R_{cat} = \frac{k_1[CO_2O_3][S(IV)]}{\{k_9[x] + k_{10}[IAA]\}} \quad (27)$$

Gupta et al proposed a similar mechanism for the COO catalysed autoxidation of sulfur dioxide inhibited by ethanol, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two [38-40]. The calculated value of inhibition constant B is 0.70×10^3 mol^{-1} L, which is in the range of 10^3 to 10^4. So on the base of calculated value of B, we concluded that iso amyl alcohol act as a free radical scavenger in the CO_2O_3 catalysed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system.

6. CONCLUSION

The role of IAAact as an inhibitor in CO_2O_3 catalysed autoxidation of SO_2 in alkaline medium has been found, and based on the observed results rate law a free radical mechanism has been proposed.

$$\frac{-d[S(IV)]}{[dt]} = \frac{(k_1 + k_2[CO_2O_3][S(IV)]}{1 + B[IAA]}$$

7. FUTURE SCOPE

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.

8. ACKNOWLEDGEMENT

The authors pay their sincere gratitude to Principal, Govt. P.G. College, Jhalawar- Rajasthan (India) for providing necessary research facilities to accomplish this study.

Conflict of Interest: This wok has no conflict of interest.

REFERENCES

1. Prasad, D.S.N., Mehta, R.K., Parashar, P., Madnawat, P.V.S., Rani, A., Singh, U., Manoj, S.V., Bansal, S.P., Gupta, K.S., (2003). Kinetics of surface-catalysed autoxidation of aqueous sulfur dioxide in cobalt (III) oxide suspensions. *J. Indian Chem. Soc.,* 80: 391-394.
2. Prasad, D.S.N., Rani, A., Gupta, K.S. (1992).Surface-catalyzed oxidation of S (IV) in aqueous silica and copper (II) oxide suspensions. *Environ. Sci. Technol.* 26: 1361-1368.
3. Gupta, K.S., Singh, R., Saxena, D., Manoj, S.V., Sharma, M., (1999). Role of manganese dioxide in the autoxidation of sulfur (IV) in oxic and anoxic suspensions *Ind. J. Chem.*, *38A*: 1129-1138.
4. Sharma, A.K. Sharma, Sharma, R. and Prasad, D.S.N., (2017). Acid rain chemistry, Catalysis and Inhibition of SO_2 in environment" ISBN 978-3-659-91204-7"LAP Lambert Academic Publishing Germany.
5. Gupta, K.S., Jain, U., Singh, A., Mehta, R.K., Manoj, S.V., Prasad, D.S.N., Sharma, A., Parashar, P., Bansal, S.P., (2004). Kinetics and mechanism of the osmium (VIII)-catalysed autoxidation of aqueous sulfur dioxide in acidic and alkaline media. *J. Indian Chem. Soc.*, *81:* 1083-1092.
6. Mudgal, P.K., Sharma, A., Mishra, C.D., Bansal, S.P., Gupta, K.S. (2008). Kinetics of ammonia and ammonium ion inhibition of the atmospheric oxidation of aqueous sulfur dioxide by oxygen. *J. Atmos. Chem.,* 61: 31-55.
7. Sharma, A.K., Prasad, D.S.N., Sharma, R., (2018). Catalysis and Inhibition of SO_2 in Atmospheric Environment- A perspective of acid rain chemistry "ISBN978-93-86841-59-9" chapter published in book entitled Analytical techniques in Chemical and biological sciences Discovery publishing house Pvt. Ltd New Delhi India.
8. Sharma, A.K., Acharya, S., Sharma, R., Saxena, M., (2012). Recovery and Reuse of SO_2 from Thermal Power Plant Emission(Chapter), in Book entitled Air Pollution - Monitoring, Modelling, Health and Control, Dr. Mukesh Khare (Ed.), ISBN: 978-953-51-0381-3, DOI: 10.5772/32390. In Tech Open Access Publisher, University campus Croatia.
9. [66] Sharma, H., Sharma, A.K., Kumar, M. and Prasad, D.S.N. (2019). The Influence of Succinic Acid on the Kinetics of the Atmospheric Oxidation of Dissolved SO2 Catalysed by Co2O3. *International Journal on Emerging Technologies*, 10(3): 82-86.
10. Manoj, S.V., Mishra, C.D., Sharma, M., Rani, A., Jain, R., Bansal, S.P., Gupta, K.S., (2000). Iron, manganese and copper concentrations in wet precipitations and kinetics of the oxidation of SO_2 in rain water at two urban sites, Jaipur and Kota, in western India. *Atmos. Environ., 34:* 4479-4486.
11. Ghosh, M. K., and Rajput, S.K. (2012).Kinetics and Mechanism of Lanthanum (III) Catalysed Oxidation of D-galactose by Cerium (IV) in Aqueous Acidic Medium, *J Applicable Chem*., *1*(4): 541-550.
12. Meena,, V., Dayal,Y.,Saxena, D. , Rani, A., Chandel, C.P., Gupta, K.S., (2016).The influence of diesel—truck exhaust particles on the kinetics of the atmospheric oxidation of dissolved sulfur dioxide by oxygen. *Environ Sci Pollut Res.,* 23(17): 17380-92.
13. Meena, V., Dayal, Y., Rathore, D.S., Chandel, C.P., Gupta, K.S., (2017). Inhibition of Aquated Sulfur Dioxide Autoxidation by Aliphatic, Acyclic, Aromatic,and Heterocyclic Volatile Organic Compounds *Int. J. Chem. Kine. 49*(4): 221-233.
14. Meena,, V., Dayal,Y., Rathore, D.S., Chandel, C.P., Gupta, K.S., (2017).Inhibition of atmospheric aqueous phase autoxidation of sulphur dioxide by volatile organic compounds: mono-, diandtri-substituted benzenes and benzoic acids. *Prog. React Kinet and Mech.,* 42(2): 111–125.
15. Wilkosz, I., Mainka, A., (2008). Mn (II)-catalysed S (IV) oxidation and its inhibition by acetic acid in acidic aqueous solutions. *J Atmos. Chem.,* 60: 1-17.

16. Ziajka, P. and Pasiuk-Bronikowska, W., (2003). Autoxidation of sulfur dioxide in the presence of alcohols under conditions related to tropospheric aqueous phase, *Atmos. Environ,* 37: 3913-3922.
17. Podkrajsek, B., Grgic, I., Tursic, J., Bercic, G., (2006). Influence of atmospheric carboxylic acids on catalytic oxidation of sulfur (IV). *J Atmos. Chem.,* 54: 103-120.
18. Gupta, K.S. (2012). Aqueous phase atmospheric oxidation of sulfur dioxide by oxygen: role of trace atmospheric constituent's metals, volatile organic compounds and ammonia. *J. Indian Chem. Soc.,* 89: 713-724.
19. Sharma, A.K., Sharma, R., Prasad, D.S.N., Parashar, P. and Gupta, A.K. (2015).Formic Acid inhibited Ag (I) Catalysed Autoxidation of S (IV) in Acidic Medium, *J. Chem. Chem. Sci.,* 5(12): 760-771.
20. Sharma, A.K., Sharma, R., Prasad, D.S.N., Parashar, P. and Gupta, A.K. (2016). Ag (I) catalyzed autoxidation of S (IV) and its inhibition by isopropyl alcohol in acidic medium.*Chem. Sci. Rev. Lett.,* 17(5): 14-23.
21. Sharma, A.K., Sharma, R., Prasad, D.S.N., (2015). Kinetics and mechanism of uncatalysed and Ag (I) catalysed autoxidation of S (IV) and its inhibition by isoamyl alcohol in acidic aqueous solutions, *Int. J. Mod. Sci. Eng. Technol*., 2(12): 31-40.
22. Sharma, A.K., Sharma, R., Prasad, D.S.N., Parashar, P. (2016). The Inhibitive action of Aniline on the autoxidation of sodium sulfite in acidic medium. *J. Anal. Phar. Res.,* 17(5):14-23.
23. Sharma, A.K., Sharma, R., Prasad, D.S.N.,(2017). The effect of atmospheric aromatic amides on the Ag (I) catalyzed S (IV) autoxidation in aqueous solution. *The Experiment,* 40(1): 2354-2363.
24. Sharma, A.K., Sharma, R., Prasad, D.S.N., Parashar, P. (2017). Ag (I) catalyzed oxidation of S(IV) in aqueous solution differing effect of benzoate ions in acidic medium, *Curr. Phy. Chem.* 7(2):338-347.
25. Sharma, A.K. and Prasad, D.S.N. (2017). Influence of pH and Organics on Autoxidation of S(IV)Catalyzed by Ag (I). *Recent Adv. Petrochem Sci.,* 3(1): 1-2.
26. Prasad, D.S.N., Rani, A., Madnavat, P.V.S., Bhargava, R., Gupta, K.S. (1991). Kinetics of surface catalyzed oxidation of sulfur (IV) by dioxygen in aqueous suspensions of cobalt (II) oxide. *J. Mol. Catal.,* 69: 395-405.
27. Sharma, H., Sharma, A.K. and Prasad, D.S.N. (2018). Kinetics and Mechanism of oxalic acid inhibited and heterogenous CO_2O_3catalysed autoxidation of S (IV) in atmospheric water. *J app Chem.* 7(5): 1442-1449.
28. Hussain, F., Begam, S., Singh, J., Sharma, A.K. and Prasad, D. S. N. (2018). Kinetics of aniline inhibited uncatalysed and CO_2O_3catalysed autoxidation of S (IV) in atmospheric environment. *Asian J Chem. Env. Res.*11: 60-67.
29. Hussain, F., Begam, S., Sharma, A.K. and Prasad, D. S. N. (2018). Effect of isopropyl alcohol on autoxidation of S (IV) catalyzed by CO_2O_3 in alkaline medium. *Bull. Pure appl. Sc.* 37(1): 9-18.
30. Hussain, F., Begam, S., Sharma, A.K. and Prasad, D. S. N. (2018). Co_2O_3 catalyzed oxidation of SO_2 in aqueous solution differing effect of benzamide in alkaline medium. *Chem. Sc. Trans.,* 7(4): 600-609.
31. Hussain, F., Begam, S., Sharma, A.K. and Prasad, D. S. N. (2018). Kinetics and Mechanism of Co_2O_3 catalysed autoxidation of sulphite and inhibition by sodium benzoate, *J. Inst. Chemists (India)* 90(4):104-119.
32. Begam, S., Hussain, F., Singh, J., Sharma, A.K. and Prasad, D.S.N. (2018).Kinetics of sodium sulphite oxidation catalyzed by Co_2O_3 and inhibited by ethylene glycol. *Asian J res chem.,* 11(3): 610-616.
33. Sharma, H., Sharma, A.K., Parashar, P. and Prasad, D.S.N. (2019). Effect of acetic acid on Co_2O_3 catalyzed autoxidation of aqueous sulphur dioxide in alkaline medium *Sch. Acad. J. Biosci*. 7(3): 117-124.
34. Sharma, A.K., Sharma, R., Prasad, D.S.N. (2017). Role of organics in Atmospheric Catalytic Autoxidation of Aqueous Sulphur Dioxide in acidic Medium. *Malaysian J. Chem.* 19(1):1–12.
35. Sharma, A.K., Sharma, R. and Prasad, D.S.N. (2017). Kinetics of isoamyl alcohol and aniline inhibited uncatalysed and Ag (I) catalysed autoxidation of S (IV) in acidic Medium. *Asian J. Res. Chem.,* 10(3): 251-258.

36. Sharma, A.K., Sharma, R. and Prasad, D.S.N. (2018). Effect of Aliphatic Mono Carboxylic acids and alcohols on Ag (I) Catalyzed oxidation of SO_2 in aqueous solution, *J Mat. Env. Sci.* 9(6): 1829-1837.
37. Bhargava, R., Prasad, D.S.N., Rani, A., Bhargava, P., Jain, U., and Gupta, K.S. (1993). Kinetics of autoxidation of aqueous sulphur dioxide in suspensions of nickel (III) oxide. *Transit. Metal Chem.*, 17: 238-241.
38. Sharma A.K. Kinetics and Mechanism of the Silver (I)-Catalyzed Autoxidation of SO2 in Aqueous Solution and Its Inhibition by Benzoate and Amide Ions (2018) *Bulletin of Pure and Applied Sciences.* 37 C (2):, 82-92.
39. Sharma, A.K., and Prasad, D.S.N. (2020). Copper Catalyzed Autoxidation of Sulphur Di Oxide and Inhibition by Methanoic Acid. Current Phy chem. *10*, 33-46.
40. Sharma, H., Sharma, A.K. and Prasad, D.S.N. (2019). Dynamics Of Malonic Acid Inhibited Uncatalysed And Co_2O_3catalysed Autoxidation Of S (IV) In Alkaline Medium. Think India Journal. 22(14): 7168-7181.