THINK INDIA JOURNAL

ISSN:0971-1260
Vol-22- Issue-14-December-2019

Dynamics Of Malonic Acid Inhibited Uncatalysed And Co_2O_3catalysed Autoxidation Of S (IV) In Alkaline Medium

H. Sharma, A. K. Sharma, and D. S. N. Prasad*.
Department of Chemistry
Govt. P. G. College, Jhalawar- 326001, Rajasthan (India)

ABSTRACT:

The kinetics of the malonic acid inhibited Co_2O_3catalysed autoxidation of S (IV) in alkaline medium has been studied and based on the observed results rate law and a free radical mechanism has been proposed.

$$\frac{-d\,[S(IV)]}{[dt]} = \frac{(k_1 + k_2[Co_2O_3])\,[S(IV)]}{1 + B\,[\text{Malonic acid}]}$$

Keywords: Kinetics; Autoxidation; SO_2; Co_2O_3; Catalysis; Inhibition; malonic acid

I. INTRODUCTION

The acid rain problem is mainly attributed to anthropogenic sulfur dioxide and, to a lesser extent, nitrogen oxide emissions. The transformation of sulfur dioxide to acid sulfate is the major cause of atmospheric acid precipitation. It is generally agreed that the gas phase oxidation including photochemical oxidation by O_3 and H_2O_2 ,which are produced in the atmosphere by photochemical reactions , and oxidation by O_2 in aqueous phase catalysed by dissolved trace metal ions and by suspended particulate matter are major contributors to acid precipitation [1-5]. The oxidation of sulfur dioxide has been one of the most frequently studied reactions in aqueous atmospheric droplets. Three reaction pathways are considered to be dominantly responsible for oxidation of SO_2 in atmospheric water droplets. These are the oxidation of dissolved SO_2 by H_2O_2, O_3 and O_2 in the presence of transition metal ions as catalysts [6-7]. The role of O_3 becomes more important above pH 6 [8]. Oxidation by molecular oxygen may also be important if cloud water contains sufficient amount of transition metal ions (e.g., Fe, Mn) for autocatalytic reactions to occur [9].

Iron(II/III) and manganese (II/III) are the most important catalysts in atmospheric droplets [10-11]. These metals are the only efficient catalysts at low pH. Other transition metals such as Cu(II), Co(III), Sc(III), Ti(III), V(II) and Cr(III) are also catalysts, but with a substantially lower effect on the reaction rate [12-13].

Recent studies show that the sulfur (IV) oxidation in atmospheric water droplets can be affected by other reactions. Organic compounds may dissolve into water droplets and react with sulfoxy radicals and transition metal ions, and thus alter the rate of catalytic S(IV) oxidation [14-20]. 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 [21-22]. It has been established that mono-carboxylic acids inhibit the oxidation, with the strongest influence found for formic acid. The lowest inhibition was caused by acetic acid [23-25].

ISSN:0971-1260
Vol-22- Issue-14-December-2019

In Indian sub-continent the pH of the rain water lies in the range 6.5-8.5. This necessitates a study of the sulfur(IV) autoxidation in the alkaline pH range. In most of the studies the role of organics has been reported in the metal ion catalysed autoxidation of sulfur(IV) in aqueous medium [26-27]. Very few studies are available on the role of organics on the metal oxide catalysed autoxidation of sulfur(IV) in aqueous medium. This led us to investigate the kinetics of sulfur(IV) autoxidation catalyzed by Co_2O_3in the pH range 7.8-9.4. and the effect of malonic acidhas been studied in alkaline media to delineate the nature of the mechanism.

II. EXPERIMENTAL

The experimental procedure was exactly the same as described earlier [28-30]. and is briefly given here. All chemicals used were of reagent grade and their solutions were prepared in double distilled water. The reactions were conducted in 0.15-L Erlenmeyer flasks, open to air and to allow the passage of atmospheric oxygen. The flask was placed in a beaker, which had an inlet at the lower part and an outlet at the upper part for circulating thermostatic water for maintaining the desired temperature, 30. ± 0.1 ^{o}C. The reactions were initiated by adding the desired volume of standard Na_2SO_3 solution to the reaction mixture containing other additives such as buffer and catalyst oxide. The reaction mixture was stirred continuously and magnetically at 1,600 ± 100 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics were studied in buffered medium, in which the pH remained fixed throughout the entire course of reaction. For this purpose, 10 cm^3 of buffer made from Na_2HPO_4 (0.08 mol L^{-1}) and KH_2PO_4 (0.02 mol L^{-1}) for alkaline medium were used (total volume 100 cm^3) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) eudiometrically in slightly acidic medium as described earlier. The reproducibility of the replicate measurements was generally better than ± 10%. All calculations were performed in MS Excel [31].

III. PRODUCT ANALYSIS

The qualitative tests showed sulfate to be the only oxidation product. For quantitative analysis, the reaction mixtures containing catalyst and S(IV) in appropriately buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of sulfur(IV). When the reaction was complete, Co_2O_3 was filtered out and sulfate was estimated gravimetrically by precipitating sulfate ions as $BaSO_4$ using standard procedure [32].

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

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

IV. 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 7.90-9.45 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, plots are shown in the Fig. 1

ISSN:0971-1260
Vol-22- Issue-14-December-2019

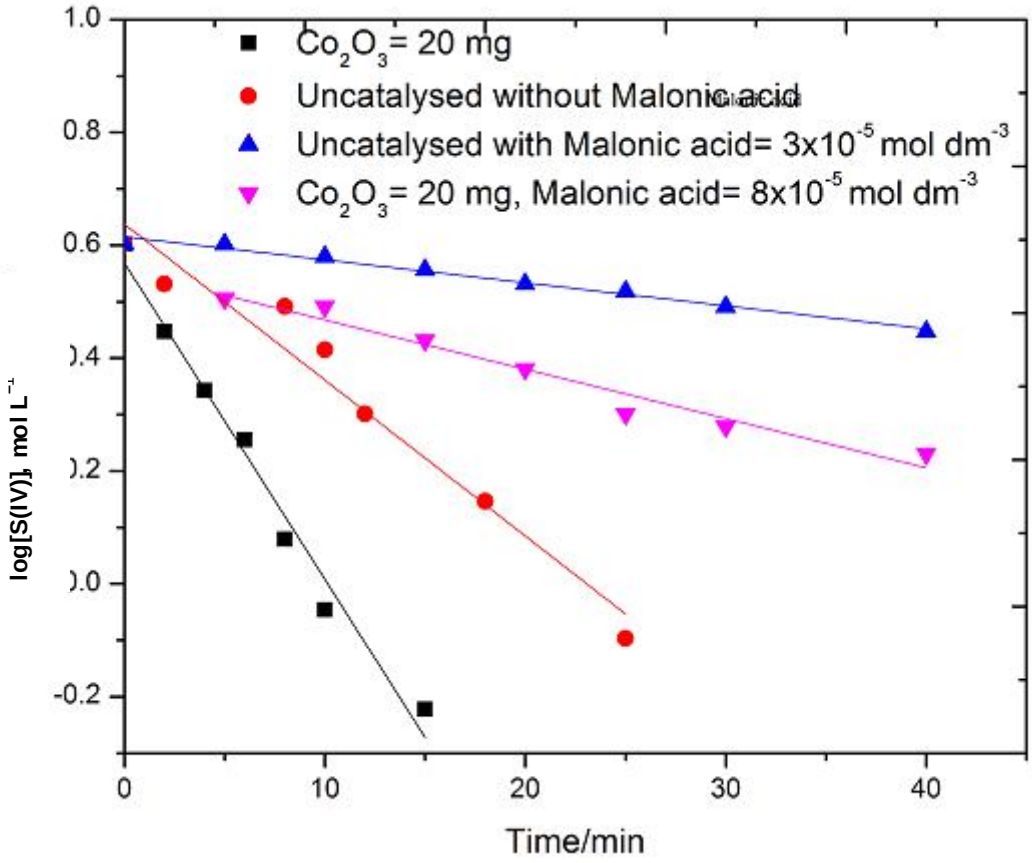

Fig. 1 The disappearance of [S(IV)] with time in air - saturated suspensions of 100 ml at [S(IV)] = 2×10^{-3} mol L^{-1}, at 30° C and pH = 7.90,

Uncatalysed Reaction

In this study the reaction was studied without adding Co_2O_3. As it is well known that the uncatalysed reaction is initiated by the trace metal ion impurities present in the reagent samples and distilled water used for the preparation of solutions, so the uncatalysed reaction is initiated by these trace metal ion impurities particularly transition metal ions.

[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 = 7.90 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.

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

ISSN:0971-1260
Vol-22- Issue-14-December-2019

Table -1 The values of k_1 for Uncatalysed reaction $_{at}$ different [S(IV)] at pH= 7.90 and t = 30^0C

[S(IV)]mol L^{-1}	$10^4 k_1$ s^{-1}
0.001	1.07
0.002	1.05
0.004	1.03
0.006	1.02

[Malonic acid] 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 malonic acid was chosen as the organic inhibitor. On varying the [malonic acid] from 1×10^{-7} 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 malonic acid did not change and remained first order. The first order rate constant k_{inh} in the presence of malonic acid was defined by the following rate law (3)

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

The values of k_{inh} at different [malonic acid] are given in table 2

Table-2 The value of k_{inh} at [S(IV)] = 2×10^{-3} mol L^{-1}, pH= 7.90, t = 30°C,

[Malonic acid]	k_{inh}	$1/k_{inh}$
0	0.0000001	2457
1×10^{-7}	0.0000002	2770
2×10^{-6}	0.0000004	3378
3×10^{-5}	0.0000006	4255
4×10^{-4}	0.000002	5076

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

$$k_{\mathrm{inh}} = k_1 / (1+B\,[\mathrm{Malonic\ acid}]) \qquad (4)$$

where B is inhibition parameter for rate inhibition by malonic acid.

By rearranging the equation (4) we get

$$1/k_{\mathrm{inh}} = 1/k_1 + B\,[\mathrm{Malonic\ acid}]/k_1 \qquad (5)$$

ISSN:0971-1260
Vol-22- Issue-14-December-2019

In accordance with eq.(5) the plot of $1/k_{inh}$ versus [malonic acid] 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 **1.05×10^{3} s** and **2.95×10^{8} mol^{-1}L** at pH = 7.90, and t=30ºC. The value of slope/intercept gives us the value of inhibition parameter B, which was found to be **3.54×10^{5} mol^{-1} L**.

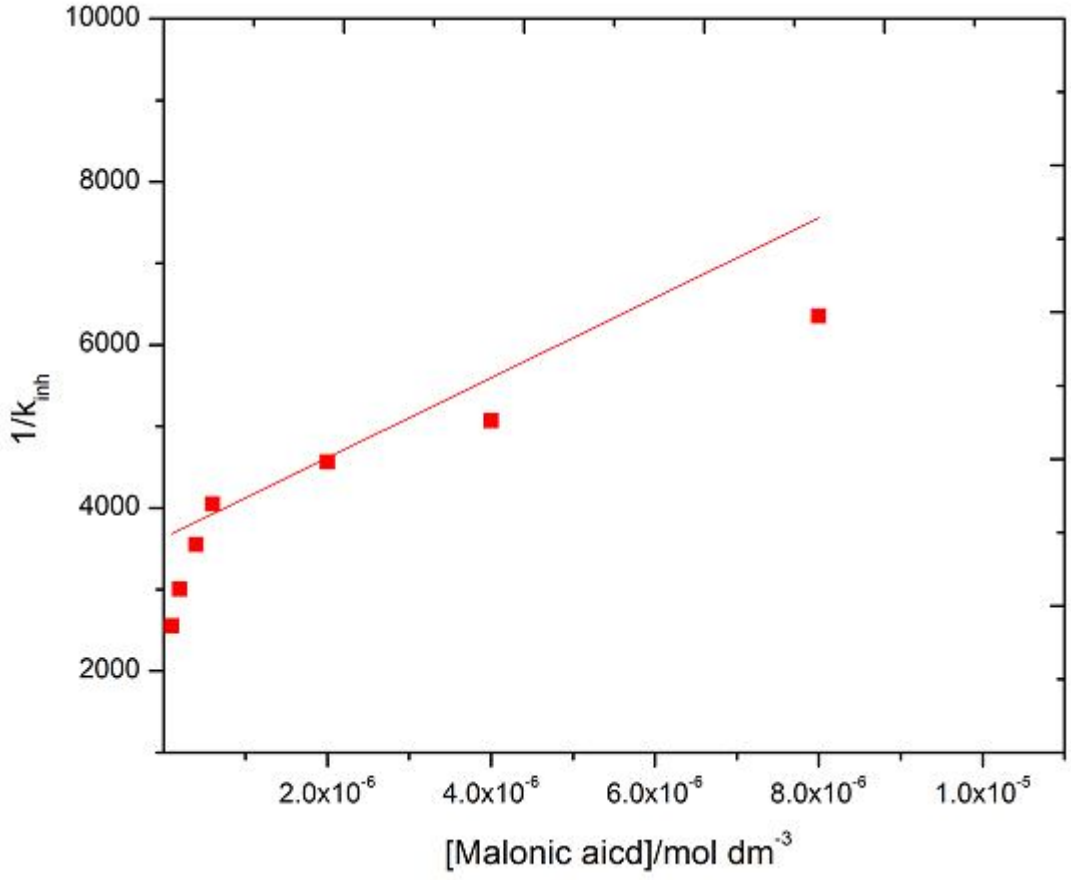

Fig. 2 Effect of malonic acid at [S(IV)] = 2×10^{-3} mol L^{-1} and at 30°C in phosphate buffered medium

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 malonic acid.

[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 = 7.90 and t=30°C. The kinetics was found to be first order in[S(IV)] as shown in Fig. 1 and log [S(IV)] versus time plots were linear.

[Co_2O_3] Variation

ISSN:0971-1260
Vol-22- Issue-14-December-2019

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=7.90 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 = 7.90 and t = 30ºC

Co_2O_3(g L^{-1})	10^3k_{cat} s^{-1}
0.1	3.04
0.2	3.52
0.3	4.24
0.4	4.79

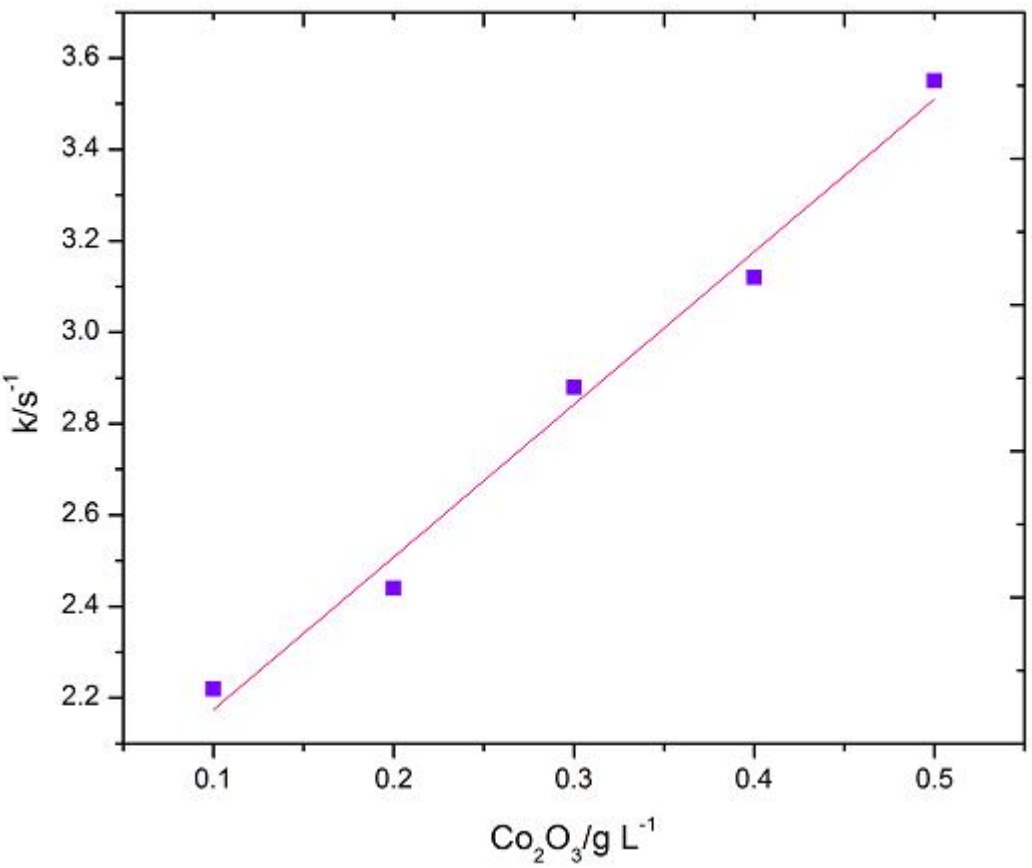

Fig. 3 The dependence of rate on catalyst concentration at [S(IV)] = 2×10^{-3}mol L^{-1}, at t=30°C and pH = 7.90

The nature of dependence of k_{cat}on $[Co_2O_3]$ shown in Fig 3 indicates the operation of a two term rate law

ISSN:0971-1260
Vol-22- Issue-14-December-2019

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

$$k_{cat} = k_1 + k_2[Co_2O_3] \quad (7)$$

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= 7.90 and 30°C.

Variation of pH

Variation in pH in the range 7.90 to 9.45 in phosphate buffer medium showed the rate to be independent of pH. The results are given in table 4. 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.

Table. 4 variation of pH at $[Co_2O_3]$ = 0.2 g L^{-1}, [malonic acid] = 2×10^{-4}mol L^{-1}, [S(IV) = 2×10^{-3}mol L^{-1} and t = 30ºC

[S(IV)]molL^{-1}	$[Co_2O_3]$ g L^{-1}	[malonic acid] molL^{-1}	pH	temp.	$10^4 k_{cat}$ $k_1 + k_2[Co_2O_3]$
0.002	0.2	0.0002 M	7.90	30°C	3.62
0.002	0.2	0.0002 M	8.15	30°C	3.58
0.002	0.2	0.0002 M	8.55	30°C	3.48
0.002	0.2	0.0002 M	9.45	30°C	3.10

Variation of Malonic acid

To know the effect of malonic acid on Co_2O_3catalysed autoxidation of S(IV), malonic acid variation was carried out from 1×10^{-4} to 4×10^{-4}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 = 7.90 and t=30°C.The results indicates that by increasing the [malonic acid] 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 malonic acidrevealed that the kinetics remain first order both in [S(IV)] and $[Co_2O_3]$ and independent of pH.

ISSN:0971-1260
Vol-22- Issue-14-December-2019

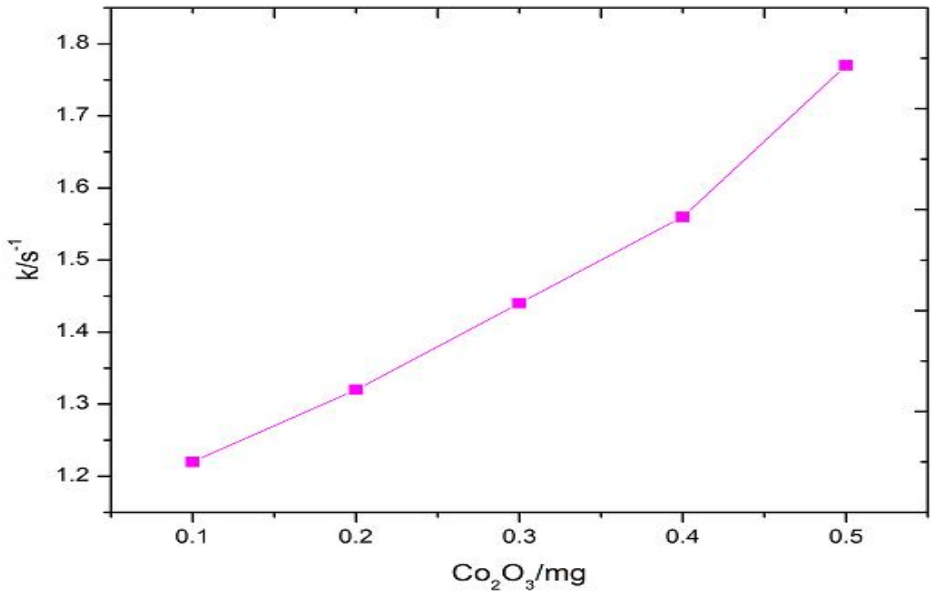

Fig. 4 Effect of [S(IV)] at malonic acid = 2×10^{-4} g L^{-1}, pH=7.90 and at 30°C, in phosphate buffered medium

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 **1.05 × 10^{-4} s^{-1}** and **1.85 × 10^{-5} g^{-1} L s^{-1}** respectively. Depend upon the observed results the reaction follows the following rate law in the presence of malonic acid.

$$-d\left[S(IV)\right] / dt = (k_1 + k_2\left[Co_2O_3\right]\left[S(IV)\right] / 1 + B\left[\text{Malonic acid}\right] \quad (8)$$

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

$$1/ k_{inh} = 1 + B\,[\text{Malonic acid}] / k_{cat} \quad (10)$$

$$1/ k_{inh} = 1/ k_{cat} + B\,[\text{Malonic acid}] / k_{cat} \quad (11)$$

By plotting a graph between $1/K_{inh}$ v/s [malonic acid] gives a linear line with non-zero intercept fig. 5. The value of intercept = $1/k_{cat}$ and slope=B/k_{cat} from the graph these values are found to be **1.85× 10^3 s** and **5.81× 10^7 mol^{-1} L s** respectively. From these values the value of inhibition parameter B can be calculated, inhibition parameter B = slope/intercept that is B = **2.81× 10^5 mol^{-1} L**.

ISSN:0971-1260
Vol-22- Issue-14-December-2019

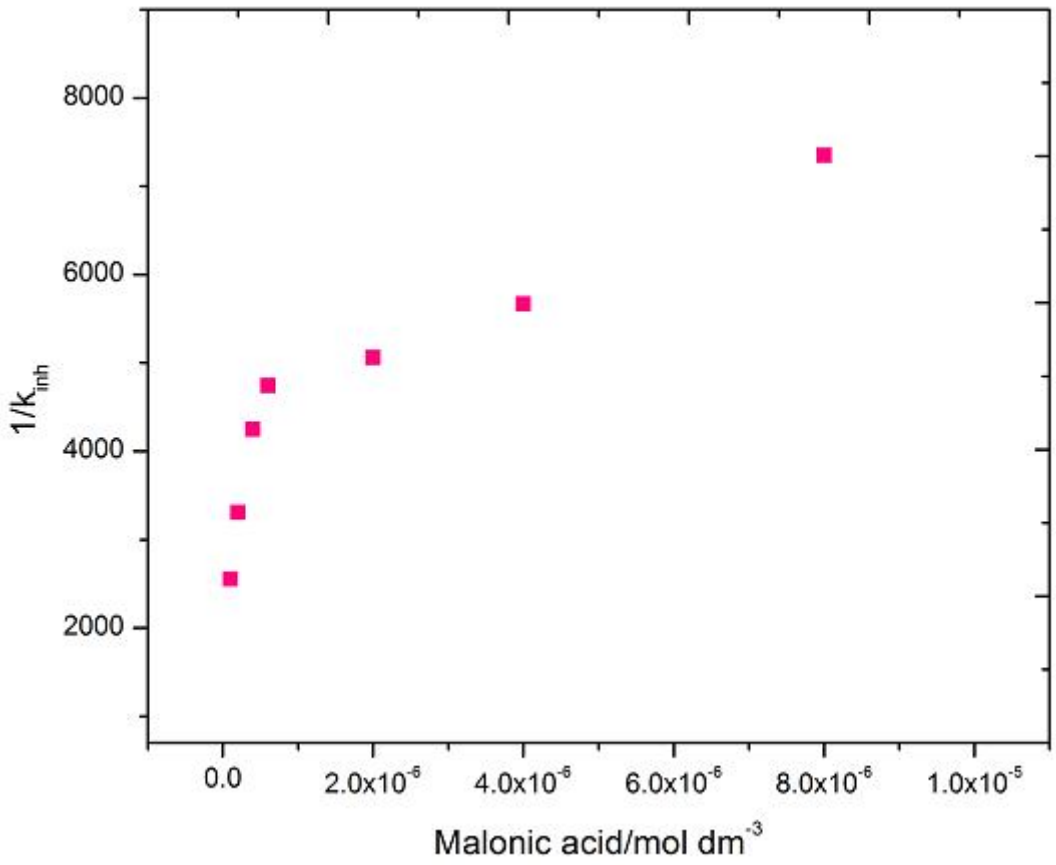

Fig. 5 Plot of $1/k_{inh}$v/s [malonic acid] at [S(IV)] = 2×10^{-3}mol L^{-1}, t = 30°C, [Co_2O_3] = 10mg, and pH = 7.90 in phosphate buffered medium.

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 24.12 kJ mol^{-1}.

Table5 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}, [malonic acid] =2×10^{-4}mol L^{-1},t = 30°C, and pH = 7.34.

t °C	10^4 k_{obs},s^{-1}
30	3.61
35	5.1
40	7.35

ISSN:0971-1260
Vol-22- Issue-14-December-2019

V. **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.

$$SO_2 + H_2O \xrightleftharpoons{K_H} SO_2.H_2O(aq.) \quad (12)$$

$$SO_2.H_2O(aq.) \xrightleftharpoons{K_1} HSO_3^- + H^+ \quad (13)$$

$$HSO_3^- \xrightleftharpoons{K_2} SO_3^- + H^+ \quad (14)$$

$$2HSO_3^- \xrightleftharpoons{K_3} S_2O_5^{-2} + H_2O \quad (15)$$

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 25ºC the values are K_H = 1.23 mol $L^{-1}atm^{-1}$, $K_1=1.4\times10^{-2}$, $K_2=6.24\times10^{-8}$, and $K_3=7.6\times10^{-2}$. In this experimental study in pH range (7.90 - 9.45), 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. Grgic*et al*.(1998, 1999); Wolf *et al*. (2000) found that oxalate has strong inhibiting effect on S(IV) autoxidation in the presence of Fe(III) or Fe(II), however oxalate has weak inhibiting effect on Mn(II) catalysed autoxidation of S(IV), because oxalate is not a strong chelating agent, Podkrajsek et al. reported that mono-carboxylic acids inhibit the oxidation, out of which formic acid shows strong inhibiting effect. The probable reason for the inhibition is the interaction between sulfate radicals and carboxylic acid. Organic compound that do not form strong complexes have also been shown an inhibiting effect on Fe(III)-catalysed oxidation of S(IV) at high pH. Martin *et al*. found that acetate and formate ions shows substance inhibiting effect at pH ≥ 5 but negligible inhibition at pH ≤ 3.

In several transition metal oxide catalysed heterogeneous aqueous phase auto oxidation reactions of sulfur(IV), the formation of surficial complexes by adsorption of sulfur(IV) and O_2 on the particle surface and oxidation of sulfur(IV) take place through the intervention of multiple oxidation states has been proposed. In the heterogeneous solid – liquid phase reaction of MnO_2 and S(IV), 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 malonic acid like that of ethanol reported by Gupta et al this indicates the operation of a radical mechanism involving oxysulfur free radicals, like $SO_3^{-\bullet}$, $SO_4^{-\bullet}$and $SO_5^{-\bullet}$. The inhibition is caused through the scavenging of $SO_4^{-\bullet}$by inhibitors such as ethanol and benzene, etc.

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 **1.12×10^4**, which lies in the same range.This strongly supports the radical mechanism. For the Co_2O_3 – catalysed reaction in presence of malonic acid. Based on the observed results including the inhibition by malonic acid, the following radical mechanism is proposed which similar to that proposed by Gupta et al in the ethanol inhibition of the Co Ocatalysed reaction [33-37].

ISSN:0971-1260
Vol-22- Issue-14-December-2019

$$Co_2O_3 + SO_3^{-2} \overset{K_1}{\rightleftharpoons} Co_2O_3.SO_3^{-2} \quad (16)$$

$$Co_2O_3.SO_3^{-2} + O_2 \overset{K_2}{\rightleftharpoons} Co_2O_3.SO_3^{-2}.O_2 \quad (17)$$

$$Co_2O_3.SO_3^{-2}.O_2 \xrightarrow{k_1} Co_2O_3. + SO_3^{-1} + O_2^{-1} \quad (18)$$

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

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

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

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

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

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

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

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 [21]. 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.

$$k_1[Co_2O_3(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Malonic acid}]\}\,[SO_4^{-1}] \quad (26)$$

Since the reaction is completely stopped in the presence of [malonic acid] at 1×10^{-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 presenceof highmalonic acid concentration. But this is not true and the reaction is completed seized in the presence of high concentration of malonic acid. This led us to ignore the step (18) and assume only the rate of reaction given by equation

ISSN:0971-1260
Vol-22- Issue-14-December-2019

(24).Since we observe a clean cut first order in [S(IV)], The value of K_1 [S(IV)]<<1 so the above rate law can be reduce to

$$R_{cat} = \frac{k_1 [Co_2O_3] [S(IV)]}{\{k_9[x] + k_{10}[\text{Malonic acid}]\}} \qquad (27)$$

Gupta et al and Sharma et al proposed a similar mechanism for the Co Ocatalysed 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.

The calculated value of inhibition constant B is **2.81×10^5** 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 malonic acid act as a free radical scavenger in the Co_2O_3catalysed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system.

VI. Conclusions

The role of malonic acid act as an inhibitor in Co_2O_3catalysed 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.

$$\frac{-d\,[S(IV)]}{[dt]} = \frac{(k_1 + k_2[Co_2O_3])\,[S(IV)]}{1 + B\,[\text{Malonic acid}]}$$

Based on the experimental results, rate constants and orders of the reactions were determined. The reaction order in SO_2 was pseudo-first order for both reactions in the presence and absence of malonic acid.

VII. 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.

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: Nil

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.

ISSN:0971-1260
Vol-22- Issue-14-December-2019

[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. MukeshKhare (Ed.), ISBN: 978-953-51-0381-3, DOI: 10.5772/32390. InTech 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 SciPollut Res.,*23(17):17380-92.
[13]. Meena,, V., Dayal, Y., Rathore, D.S.,Chandel, C.P., Gupta, K.S., (2017). Inhibition of AquatedSulfurDioxide 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 ofsulphur 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_3catalysed 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.

ISSN:0971-1260
Vol-22- Issue-14-December-2019

[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 (II) oxide.*Transit. Metal Chem.*, 17: 238-241.

