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Kinetics of formic acid inhibited uncatalysed and Co_2O_3 catalysed autoxidation of sulfur(IV) in alkaline medium

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ABSTRACT

The kinetics of environmentally imperative atmospheric autoxidation of sulfur(IV) by Co_2O_3 in the pH range 7.30-9.40 has been studied. The aqueous phase autoxidation of sulfur(IV) is the major factor responsible for acidification of atmospheric aqueous system. The role of formic acid as an inhibitor of Co_2O_3 catalysed autoxidation of sulfur(IV) in alkaline medium has been identified, and based on the observed results rate law and a free radical mechanism has been proposed.

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

Keywords: Alkaline medium; Autoxidation; Formic acid; Kinetics; Sulfur(IV)
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INTRODUCTION

The phenomenon of acid rain is accredited mainly to anthropogenic sulfur dioxide (SO_2), and in lesser extent, to nitrogen oxide (NO_x) emissions. The process of oxidative transformation of sulfur dioxide into sulphuric acid is the major cause of atmospheric acid precipitation [1-2]. Sulfur dioxide is vulnerable to environmental oxidation through various processes including, photochemical oxidation in gaseous phase by O_3 and H_2O_2, produced in the atmosphere by photochemical reactions; oxidation caused by O_2 in aqueous phase catalysed by dissolved trace metal ions, and by suspended particulate matters. All these processes have shown major contribution in acid precipitation [3-4]. The metal oxides released to the atmosphere as a result of combustion processes are therefore important constituents of suspended. The catalytic role of several metal oxides such as CoO, Co_2O_3, Ni_2O_3, CuO, MnO_2 and Cu_2O in acidic medium has been reported [5-10]. In general the kinetics agreed with the rate law (1).

$$- d[S(IV)]/dt = (k_1 + k_2[H^+]^{-1})\,[\text{Catalyst}]\,[S(IV)] \qquad (1)$$

Where, k_1 and k_2 are the rate constants for the autoxidation of HSO_3^- and SO_3^{2-}, respectively.

In the mechanism, formation of surficial complexes by adsorption of sulfur(IV) and O_2 on particle surface followed by subsequent oxidation of former by latter via a non-radical mechanism has been proposed. Herrmann et al. reported that the interaction between alcohols and SO_2 oxidation intermediates may have a bearing on acidity formation in the atmosphere [11]. Alyea and Backstrom [12] studied the inhibiting effect of aliphatic alcohols on the oxidation of sodium sulphite in alkaline medium (pH 8.4). Later, Backstrom proposed a radical mechanism for the autoxidation of S(IV) to show the probable contribution of radicals such as $SO_3^{-\bullet}$, $SO_4^{-\bullet}$ and $SO_5^{-\bullet}$ in the

formation of a chain and to explain the alcohol inhibition[13]. The sulfur(IV) autoxidation reaction is known to proceed via both radical and non-radical mechanisms [14-17]. An interesting feature of many radical reactions is the inhibition of reaction rate by organics such as acetic acid, oxalic acid [18], alcohols [19], Carboxylic acid [20] and ethanol [21].

Worldwide, it is observed that the pH of the rain water is generally laid in the range 6.5-8.5 [2, 22-23]. This necessitates the study of autoxidation of sulfur(IV) in alkaline medium. This led us to investigate the kinetics of sulfur(IV) autoxidation catalysed by Co_2O_3 in the pH range 7.3-9.4, and so the effect of formic acid on this reaction has been studied to know the nature of mechanism.

MATERIALS AND METHODS

The chemicals were of analytical reagent grade and their solutions were prepared in double distilled water. The experimental procedure [5-10] was adopted for the present study. Briefly, the reactions were conducted in 0.15L 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, $303 \pm 0.1K$. 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 $1,600 \pm 100$ rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The kinetics was studied in buffered medium, in which the pH remained fixed throughout the entire course of reaction. For this purpose, the alkaline buffer made from Na_2HPO_4 (0.08 mol L^{-1}) and KH_2PO_4 (0.02 mol L^{-1}) was used to obtain the desired pH. The kinetics was studied by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically, in slightly acidic medium as described earlier. The reproducibility of the replicate measurements was found better than $\pm10\%$. All calculations were performed in MS Excel.

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 [24].

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

$$S(IV) + 0.5O_2 \longrightarrow S(VI) \qquad\qquad\qquad (2)$$
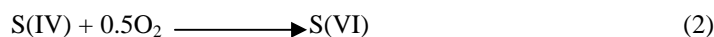
RESULTS AND DISCUSSION

The kinetics of uncatalysed and Co_2O_3 catalysed autoxidation reaction of S(IV) was studied in alkaline medium in the pH range 7.34-9.40 at 303K. In both cases, the reaction followed the first order kinetics for [S(IV)]. The kinetic data were based on the determination of first order rate constant k_1 from the plot of log [S(IV)] versus time 't' (Fig. 1).

Uncatalysed Reaction
The uncatalysed reactions are generally initiated by the impurities and traces of metal ions, particularly transition metal ions present in the reagents and solutions [21]. The dependence of the reaction rate on [S(IV)] was studied by varying [S(IV)] from 1×10^{-3} mol L^{-1} to 6×10^{-3} mol L^{-1} at pH=7.34 (T=303K) in phosphate buffer medium. The reaction was found to follow the first order kinetics, and log [S(IV)] vs. time (t) plots were linear. The values of first order rate constant k_1 have been shown in table 1.

Table 1: The values of k_1 for uncatalysed reaction at different [S(IV)] at pH= 7.34, T=303K.

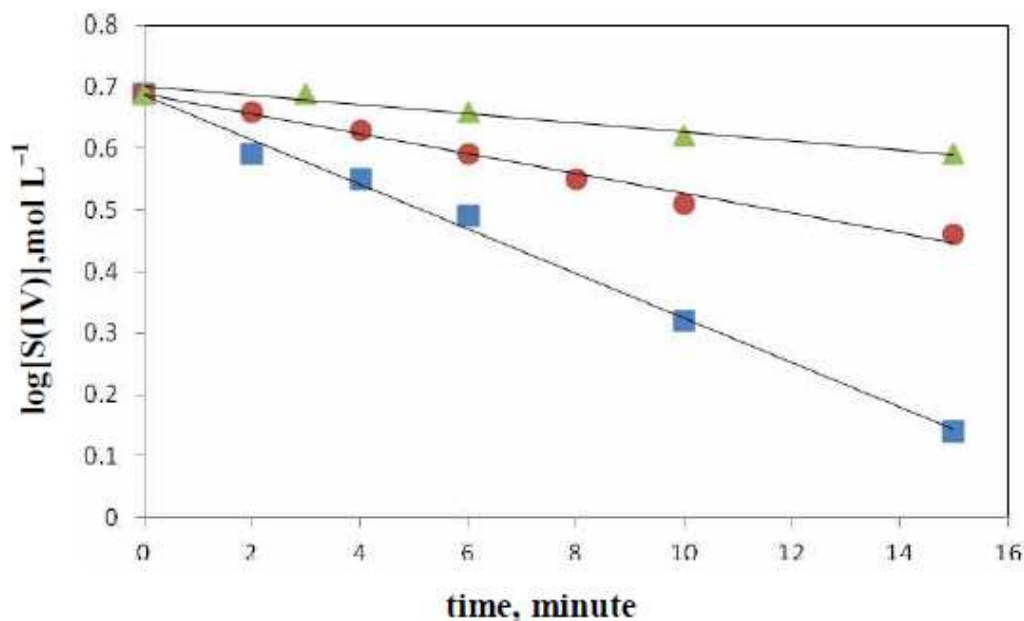| [S(IV)]mol L^{-1}	$10^4 k_1$ s^{-1}
0.001	6.15
0.002	6.19
0.004	6.32
0.006	6.11

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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}, T = 303K and pH = 7.34. (■)[Co$_2$O$_3$] = 20 mg, [formic acid] = 0 ml, (●) Uncatalysed and without formic acid (▲) [Co$_2$O$_3$] = 20mg, [Formic acid] = 6×10^{-4}mol L^{-1}.

The dependence of reaction rate on [S(IV)] is given below;

$$- \frac{d[S(lV)]}{dt} = k_1[S(IV)] \qquad (3)$$

The major aim of the present study was to examine the effect of organic inhibitors on the autoxidation of S(IV) in alkaline medium. Therefore, formic acid was chosen as an inhibitor. On varying the [formic acid] from 1×10^{-4} to 6×10^{-4} mol L^{-1}, the rate of the reaction become decelerated. In presence of formic acid, the dependence of rate law on [S(IV)] did not change and remained first order. The first order rate constant k_{inh} in the presence of formic acid was defined by the following rate law (4)

$$- \frac{d[S(lV)]}{dt} = k_{inh}[S(IV)] \qquad (4)$$

The values of k_{inh} at different concentrations of formic acid are given in table 2.

Table 2: The value of k_{inh} at [S(IV)] = 2×10^{-3} mol L^{-1}, pH= 7.34, T=303K.

[Formic acid]	k_{inh} s^{-1}	$1/k_{inh}$ s
0	6.19×10^{-4}	1616
1×10^{-4}	3.19×10^{-4}	3135
2×10^{-4}	2.66×10^{-4}	3759
4×10^{-4}	2.20×10^{-4}	4545
6×10^{-4}	1.61×10^{-4}	6211

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

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

Where, B is inhibition parameter for rate inhibition by formic acid.

By rearranging the equation (5) we get

$$1/k_{inh} = 1/k_1 + B[\text{formic acid}]/k_1 \qquad (6)$$

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In accordance with equation (6) the plot of $1/k_{inh}$ versus [formic 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 **2.06×10³ s** and **6.8×10⁶ mol⁻¹ L** at pH = 7.34, and T=303K. The value of slope/intercept gives the value of inhibition parameter B, which was found to be **3.35×10³ mol⁻¹ L**.
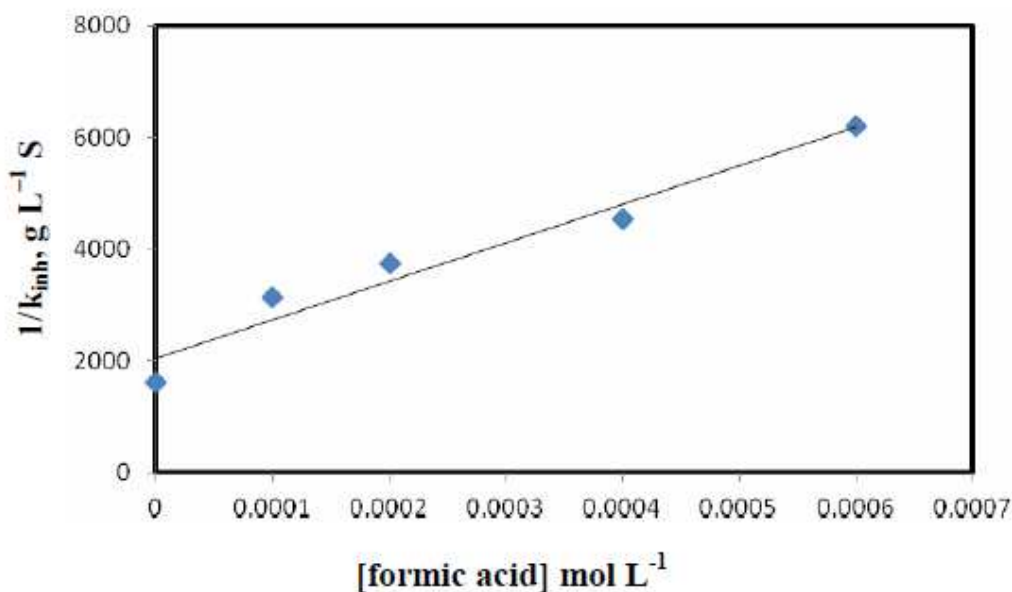

Fig. 2. Effect of formic acid at [S(IV)] = 2×10⁻³ mol L⁻¹ and T = 303K, in phosphate buffered medium.

Co₂O₃ Catalysed Reaction
The kinetics of Co₂O₃ catalysed autoxidation of S(IV) was studied in alkaline medium in the absence of inhibitor formic 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 [Co₂O₃] of 0.1 and 0.2 g L⁻¹ at pH = 7.34 and T=303K. The kinetics was found to be first order in [S(IV)] as shown in fig. 1, and log [S(IV)] versus time (t) plots were linear.

[Co₂O₃] Variation
The dependence of reaction rate on [Co₂O₃] was studied by varying [Co₂O₃] from 0.1gL⁻¹ - 0.4gL⁻¹ at fixed [S(IV)] of $2×10^{-3}$ mol L⁻¹ at pH=7.34 and T=303K in phosphate buffer medium. The values of first order rate constants k_{cat}, for S(IV) - autoxidation was determined at different [Co₂O₃], as given in table 3.

Table 3. The value of k_{cat} at different [Co₂O₃] at pH = 7.34 and T=303K.

Co₂O₃(g L⁻¹)	$10^3 k_{cat}$ s⁻¹
0.1	8.8
0.2	13.7
0.3	16.9
0.4	21.1

The nature of dependence of k_{cat} on [Co₂O₃] shown in fig. 3 indicates a two term rate law.

$$- \frac{d[S(IV)]}{dt} = k_{cat}[S(IV)] = (k_1 + k_2 [Co_2O_3]) [S(IV)] \tag{7}$$

$$\text{or} \quad k_{cat} = (k_1 + k_2 [Co_2O_3]) \tag{8}$$

From the plot in fig. 3, the values of intercept is equal to k_1 and slope is equal to k_2, which were found to be **5.1 × 10⁻⁴ s** and **4.01 × 10⁻³ mol⁻¹ L s,** respectively at pH= 7.34 and T=303K.

Variation of pH
Variation in pH in the range 7.34 to 9.4 in phosphate buffer medium showed the rate to be independent of pH. The effect of [buffer] was examined by varying the concentration of both Na₂HPO₄ & KH₂PO₄ in such a way that the

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ratio [Na_2HPO_4] / [KH_2PO_4] remained same to maintain the pH. The values showed that the rate of the reaction to be insensitive to the buffer concentration (table 4).
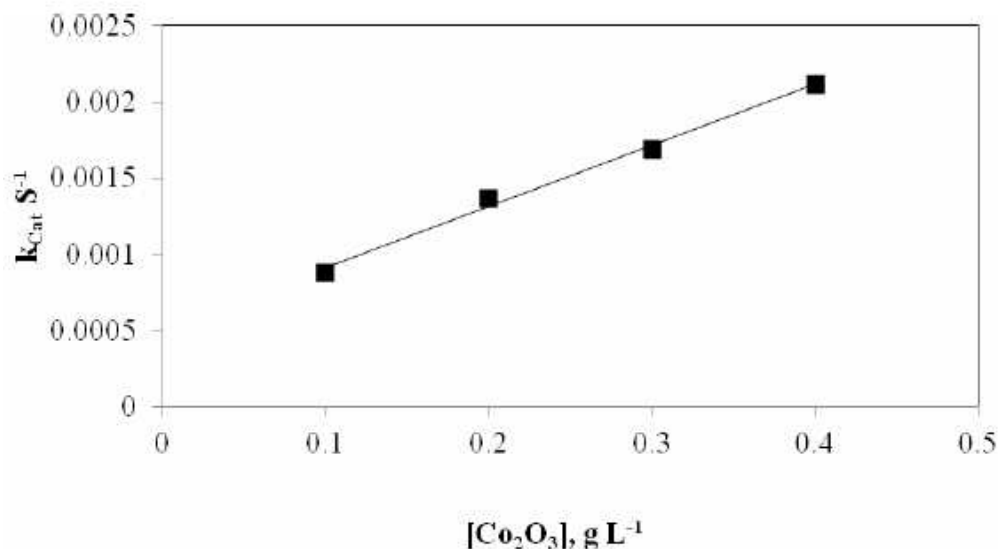

Fig. 3. The dependence of rate on catalyst concentration at [S(IV)] = 2×10⁻³ mol L⁻¹, T = 303K and pH = 7.34.

Table 4. Variation of pH at [Co_2O_3] = 0.2 g L⁻¹, [[Formic acid] = 2×10⁻⁴mol L⁻¹, S(IV) = 2×10⁻³ mol L⁻¹ and T=303K

[S(IV)]molL⁻¹	[Co₂O₃] g L⁻¹	[Formic acid] molL⁻¹	pH	Temp. (K)	10⁴kcat k₁ + k₂[Co₂O₃]
0.002	0.2	.0002 M	7.34	303	5.28
"	"	"	8.50	"	5.15
"	"	"	8.90	"	5.47
"	"	"	9.40	"	5.42

Variation of formic acid

To know the effect of formic acid on Co_2O_3 catalysed autoxidation of S(IV), formic acid variation was carried out from 0.5×10⁻⁴ to 6×10⁻⁴mol 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 = 7.34 and T=303K.The results indicates that by increasing the [formic 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 formic acid, which revealed that the kinetics remained first order both in [S(IV)] and [Co_2O_3] and independent of pH. A plot between [Co_2O_3] vs. first order rate constant is linear (fig. 4) with non-zero intercept. The value of intercept and slope are found to be **1.77 × 10⁻⁴ s⁻¹** and 1.6 × 10⁻⁵ **g⁻¹ L s⁻¹,** respectively.
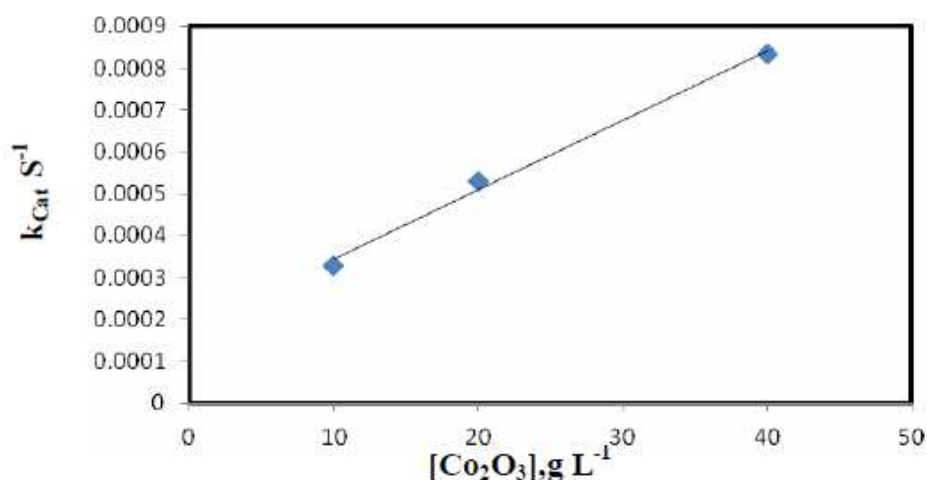
Fig. 4. Effect of [Co_2O_3] at formic acid = 2×10⁻⁴ mol L⁻¹, pH=7.34 and T=303K in phosphate buffered medium.

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Depending upon the observed results, the reaction follows the following rate law in the presence of formic acid.

$$-\frac{d[S(IV)]}{dt} = \frac{(k_1 + k_2[Co_2O_3])\,[S(IV)]}{1 + B\,[formic\ acid]} \qquad (9)$$

$$\text{Where, } k_{inh} = \frac{(k_1 + k_2[Co_2O_3])}{1 + B\,[formic\ acid]} = \frac{k_{cat}}{1 + B\,[formic\ acid]}$$

$$\frac{1}{k_{inh}} = \frac{1 + B\,[formic\ acid]}{k_{cat}}$$

$$\frac{1}{k_{inh}} = \frac{1}{k_{cat}} + \frac{B\,[formic\ acid]}{k_{cat}}$$

The graph between $1/k_{inh}$ vs [formic acid] gives a linear line with non-zero intercept (fig. 5).The values of intercept = $1/k_{cat}$ and slope=B/k_{cat} from the graph are found to be **1.70 × 10³ s** and **6.10 × 10⁶ mol⁻¹ L s** respectively. From these values the value of inhibition parameter B = slope/intercept can be calculated. For this reaction, inhibition parameter B is found to be **3.58 × 10³ mol⁻¹ L**.
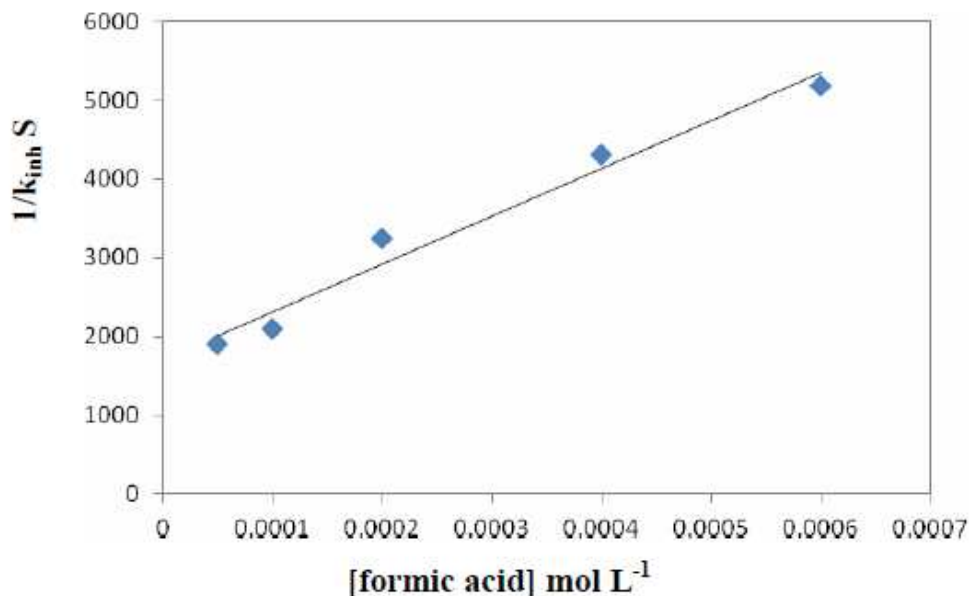
Fig. 5. Plot of $1/k_{inh}$ vs. [formic acid] at [S(IV)] = 2 × 10⁻³ mol L⁻¹, T=303K, [Co₂O₃] = 10 mg and pH = 7.34 in phosphate buffered medium.
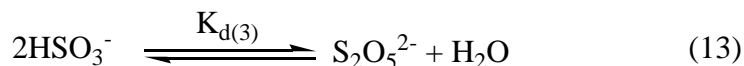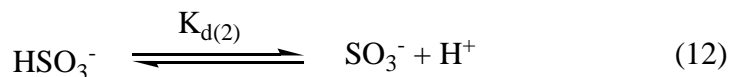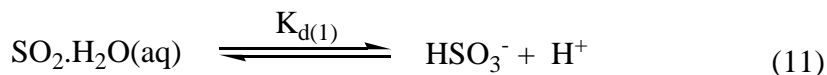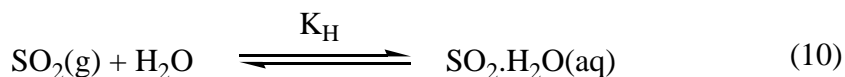
Effect of temperature
To calculate the apparent empirical energy of activation, the values of k_{obs} were determined at three different temperatures in the range 303K to 313K. The results are given in table 5. By plotting a graph between log k versus 1/t gives us the apparent energy of activation equals to 20.3 kJ mol⁻¹.

Table 5: Effect of temperature on k_{obs} air saturated suspensions at [S(IV)] = 2 × 10⁻³ mol L⁻¹, [Co₂O₃] = 0.2 g L⁻¹, [formic acid] =2×10⁻⁴ mol L⁻¹, and pH = 7.34.

T (K)	$10^4\ k_{obs}$,s⁻¹
303	5.28
308	6.88
313	8.75

DISCUSSION

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

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$$SO_2(g) + H_2O \xrightleftharpoons{K_H} SO_2.H_2O(aq) \qquad (10)$$

$$SO_2.H_2O(aq) \xrightleftharpoons{K_{d(1)}} HSO_3^- + H^+ \qquad (11)$$

$$HSO_3^- \xrightleftharpoons{K_{d(2)}} SO_3^- + H^+ \qquad (12)$$

$$2HSO_3^- \xrightleftharpoons{K_{d(3)}} S_2O_5^{2-} + H_2O \qquad (13)$$

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 (7.34 - 9.4), 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 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 [5-10] . 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 [25] In the present study, the dependence of oxygen shows the formation of surficial complex by adsorption of O_2 on the particle surface of Co_2O_3 through the fast step.
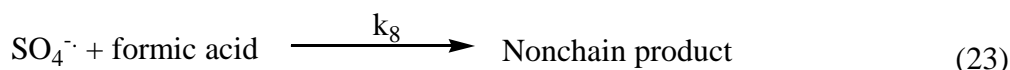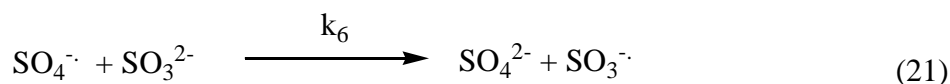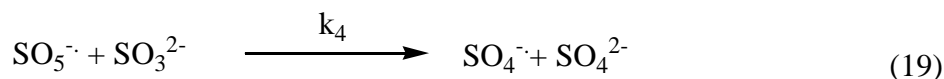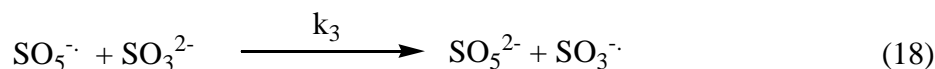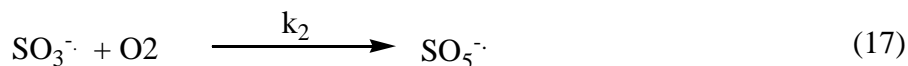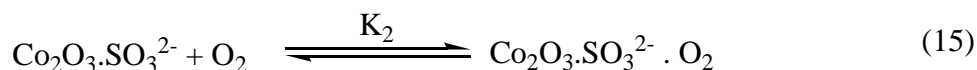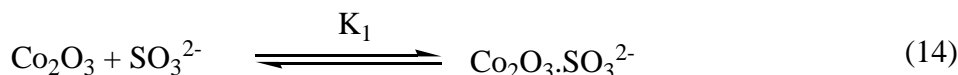
Bigelow et al. studied the effect of alcohols such as methanol, ethanol, propanol and butanol on the reaction between sodium sulphite and O_2 and found that these alcohols inhibit the reaction rate [26]. Alyea and Backstrom [12] studied the inhibiting effect of aliphatic alcohols (ethanol, isopropanol, secondary butanol and benzyl alcohol) on the autoxidation of sodium sulphite in alkaline medium(initial pH 8.4). Backstrom [14] proposed radical chain mechanism of alcohol inhibited oxidation reaction between sodium sulphite and oxygen. Connick and Zhang reported that in the presence of Mn^{+2} ions the inhibition by methanol is more complex [27]. Grgic et al. studied the inhibiting effect of oxalate, acetate and formate on the Fe-catalysed autoxidation of S(IV) at pH value 2.8, 3.7, and 4.5 and found that oxalate has a strong inhibiting effect on the reaction rate due to reduced amount of catalytically active Fe(III) ion due to the complexation with oxalate [28].

Bostjan Podkrajsek et al. [20] studied the effect of carboxylic acids on Mn(II) catalysed oxidation of sulfur(IV) and observed that mono carboxylic acids inhibit the oxidation and strongest influence found for formic acid and also observed induction period due to higher inhibition.

In alkaline medium the rate of Co_2O_3 catalysed reaction is highly decelerated by the addition of formic acid like that of ethanol reported by Gupta et al. [21]. This indicates the operation of a radical mechanism involving oxysulfur free radicals, like $SO_3^{-\bullet}$, $SO_4^{-\bullet}$ and $SO_5^{-\bullet}$ [21, 29-30]. The inhibition is caused through the scavenging of $SO_4^{-\bullet}$ by inhibitors such as ethanol and benzene, etc.

Gupta et al. [21] reported that a radical mechanism operates in those reactions in which the inhibition parameter lies the range 10^3-10^4. In the present study the value of inhibitor parameter is found to be **3.58×10^3**, which lies in the same range. This strongly supports the radical mechanism in the present reaction too. Based on the observed results including the inhibition by formic acid, a similar radical mechanism is proposed like that of Gupta et al. proposed in the ethanol inhibition of the CoO catalysed reaction [21].

In the mechanism, no role is assigned to O_2^-, which is also known to react with sulfur (IV) slowly [22]. It may disproportionate to form H_2O_2 and O_2 or may be scavenged by impurities [22]. 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.

$$Co_2O_3 + SO_3^{2-} \xrightleftharpoons{K_1} Co_2O_3.SO_3^{2-} \tag{14}$$

$$Co_2O_3.SO_3^{2-} + O_2 \xrightleftharpoons{K_2} Co_2O_3.SO_3^{2-}.O_2 \tag{15}$$

$$Co_2O_3.SO_3^{2-}.O_2 \xrightarrow{k_1} Co_2O_3 + SO_3^{-.} + O_2^{-} \tag{16}$$

$$SO_3^{-.} + O2 \xrightarrow{k_2} SO_5^{-.} \tag{17}$$

$$SO_5^{-.} + SO_3^{2-} \xrightarrow{k_3} SO_5^{2-} + SO_3^{-.} \tag{18}$$

$$SO_5^{-.} + SO_3^{2-} \xrightarrow{k_4} SO_4^{-.} + SO_4^{2-} \tag{19}$$

$$SO_5^{2-} + SO_3^{2-} \xrightarrow{k_5} 2SO_4^{2-} \tag{20}$$

$$SO_4^{-.} + SO_3^{2-} \xrightarrow{k_6} SO_4^{2-} + SO_3^{-.} \tag{21}$$

$$SO_4^{-.} + x \xrightarrow{k_7} \text{Nonchain product} \tag{22}$$

$$SO_4^{-.} + \text{formic acid} \xrightarrow{k_8} \text{Nonchain product} \tag{23}$$

(Eq. 24)

$$k_1[Co_2O_3(SO_3^{2-})(O_2)] = \{k_7[X]+k_8[\text{formic acid}]\}[SO_4^{-\bullet}] \tag{24}$$

The steps (16) & (20) appear to be unimportant because the reaction is completely seized by the presence of [formic acid] = 1.5×10^{-3}mol L^{-1}.

The contribution of propagation reaction (19) been significant in the Co_2O_3 catalysed reaction where the autoxidation reaction should have occurred even in the presence of high formic acid concentration, but this is not true and the reaction is completed seized in the presence of high concentration of formic acid. This led us to ignore the step (19) and assume only the rate of reaction given by equation (25).

$$-d[S(IV)]/dt = R_{cat} = k_6 [SO_4^{-\bullet}] [SO_3^{2-}] \tag{25}$$

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

$$R_{cat} = \frac{k_6 k_1 [Co_2O_3. SO_3^{2-}.O_2] [SO_3^{2-}]}{k_7[x] + k_8 [\text{formic acid}]} \tag{26}$$

From equilibria 14 & 15

$$R_{cat} = \frac{k_6 K_2 K_1 [Co_2O_3] [S(IV)] [O_2]}{\{1 + k_1[S(IV)] \{k_7 [x] + k_8 [\text{formic acid}]\}} \tag{27}$$

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

$$R_{cat} = \frac{k^1 [Co_2O_3] [S(IV)]}{\{1 + k_1[S(IV)]\} \{k_7 [x] + k_8 [\text{formic acid}]\}} \tag{28}$$

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

$$R_{cat} = \frac{k_1 [Co_2O_3] [S(IV)]}{[x] + k_8 [\text{formic acid}]} \tag{29}$$

Gupta et al. proposed a similar mechanism for the CoO catalysed autoxidation of sulfur dioxide inhibited by ethanol, leading to the same rate law [19]. 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 3.58×10^3 mol^{-1} L. Therefore, it is concluded that formic acid acts as a free radical scavenger in the Co_2O_3 catalysed autoxidation of aqueous sulfur dioxide in alkaline medium, and a free radical mechanism is operated in this system.

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