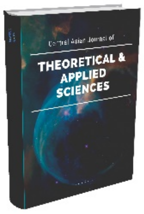

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Kinetics of the Uninhibited and Resorcinol Inhibited CoO Catalysed Autoxidation of Sulfur (IV) in Alkaline Heterogeneous Medium

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Abstract: *The kinetics of resorcinol inhibited CoO catalysed S(IV) autoxidation in the pH range 7.50 to 8.50 medium have been investigated and a rate law & free radical mechanism have been proposed based on the observed results and inhibition parameters. In all situations, the reaction's order and rate constants were calculated, meanwhile, the reaction was determined to be first-order. The impact of various temperatures & pH levels were explored also. We reported resorcinol as a significant inhibitor for SO2 autoxidation in the pH range of 7.50 to 8.80. The Arrhenius equation was used to get the value of apparent activation energy (Ea) (K= A.e-Ea/RT).*

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

INTRODUCTION

In atmospheric chemistry, one of the serious global problems is acid rain, in which the pH of the rainwater decreases. It is a common occurrence in several industrially developed countries in the northern hemisphere. Through the process of moist depositions, it has extremely detrimental effects on plants, aquatic creatures, soil, structures, and materials. Acid rain is formed by ammonium, carbon, nitrogen, and sulfur chemicals in the atmosphere reacting with water molecules to produce acids. The kinetics of dissolved sulfur dioxide oxidation has been the focus of several recent reviews due to its role in acid rain chemistry[1-3]. 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 into acids such as HNO_2, HNO_3, H_2SO_3, and H_2SO_4. The atmospheric reactions of SO_2 and NO_x etc. are major acid rain precursors and responsible for the acidification of various forms of atmospheric water[4,5].

The oxidative transformation of sulfur dioxide into sulfuric acid is the primary cause of acid precipitation in the atmosphere. Oxidation is catalysed by dissolved trace metal ions and suspended particulate particles in the aqueous phase. Which are created in the atmosphere by photochemical reactions between O_3 and H_2O_2 in the gaseous phase. A large number of organic and inorganic chemical species are released into the atmosphere by anthropogenic and natural sources. The subsequent photochemical and thermal reactions of these species in gas and aqueous phases form the backbone of atmospheric chemistry[6]. The oxidation of aqueous sulfur dioxide into acid sulfate is catalysed by trace metal ions found in all atmospheric systems.

Metal oxides are a component of suspended particulate matter (SPM) that is discharged into the atmosphere as a result of combustion activities. In this regard, the catalytic role of numerous metal oxides in acidic media, such as CoO[7], Co_2O_3[8], Ni_2O_3[9], CuO[10], MnO_2[11], and Cu_2O[12] has been thoroughly investigated. The kinetics aligned with the rate law for the first five oxides (1).

$$-d[S(IV)]/dt = (k'_1 + k''_2[H^+]^{-1})[Catalyst]\,[S(IV)] \qquad (1)$$

Where k'_1 and k''_2 are the rate constants for HSO_3^- and SO_3^{2-} autoxidation, respectively.

Rate inhibition by organics such as ethanol owing to scavenging of oxy sulfur radicals engaged in radical autoxidation is an interesting property of many radical reactions, and specifics of the process may be found in papers[13-18] and reviews[19-22]. Bigelow *et al.,* (1988)[23] postulated a radical mechanism for CoO and Co_2O_3 by preventing the CoO, Co_2O_3, and Ni_2O_3 catalysed autoxidation reaction in an alkaline medium. Aleya and Backstrom *et al.,*(1929)[24] looked researched how aliphatic alcohols including ethanol, isopropanol, secondary butanol, and benzyl alcohol hinder sodium sulfite oxidation under alkaline environments. Alcohols, which are abundantly found in both urban and rural environments, are classified as volatile organic compounds (VOCs) postulated by Hussain, F. *et al.,*.(2018)[25] and J.ziajka, W. Pasiuk-bronikowska *et al.,* (2003)[26]. Through their interactions with hydroxyl, nitrate, and sulfate radicals, they play an important role in troposphere chemistry[26,27]. The interaction of alcohols with SO_2 oxidation intermediates could have an impact on the development of acidity in the atmosphere. Organics such as acetic acid[21], oxalic acid[21], alcohols[28,29], carboxylic acid[30,31], ammonia, formic acid[32-34], aniline[35], benzamide[36], sodium benzoate[37], ascorbic acid[37], organic compounds[38], VOCs[39-42,48], and diesel truck particles[43] decrease the pace of numerous radical processes. The pH of water on the Indian subcontinent ranges from 6.5 to 8.5. This needs to research into S(IV) autoxidation in alkaline medium pH ranges.

Most studies have mentioned the role of organics in the metal ion catalysed autoxidation of S(IV) in aqueous media. The inhibitory impact of resorcinol on metal oxide catalysed aqueous sulfur dioxide autoxidation has yet to be investigated. There is very little research founded on the effect of organics on the cobalt oxide catalysed autoxidation of S(IV) in an aqueous heterogeneous alkaline solution. To characterize the nature of the process, we investigated the kinetics of S(IV) autoxidation catalysed by CoO in the pH range 7.50 - 8.50 and the influence of resorcinol in an aqueous heterogeneous alkaline media.

EXPERIMENTAL

The procedure for the experiment was the same as previously reported[41,42] and is summarized in this paragraph. A conductivity (doubled distilled) water solution was used to prepare all of the chemical solutions. A "150 ml Erlenmeyer flask" was used for the reactions, which were carried out with the lid open so that oxygen from the atmosphere could flow through. When the target temperature of $30\pm0.10^{o}C$ was desired, the flask was positioned in a beaker with an inlet at the bottom and exit at the top. Standard Na_2SO_3 solution was mixed into the reaction mixture together with buffer and catalyst (metal oxide) in the necessary volume to start the reactions. To avoid the reaction from becoming oxygen mass transfer controlled, we used a magnetic stirrer set to 1600 ±100 rpm to continually agitate the reaction mixture. There were no pH fluctuations during the experiment, which allowed for a better understanding of how reactions proceed. To achieve the necessary pH, 100 ml of buffer containing 10 cm^3 of Na_2HPO_4 (0.08 mol dm^{-3}) and KH_2PO_4 (0.02 mol dm^{-3}) alkaline medium was utilized. Aliquots of S(IV) were taken occasionally and titrated iodometrically in slightly alkaline media to monitor the kinetics. Replica measurements were frequently within +10% of each other in terms of accuracy. MS Excel-2010 was used for all calculations and graphs in the trials.

PRODUCT ANALYSIS

Sulfate was found to be the only product of oxidation in the qualitative tests. "The reaction mixtures containing catalyst and S(IV) in appropriately buffered solutions were constantly stirred for a sufficiently long time to ensure complete oxidation of sulfur(IV)," according to the quantitative analysis. CoO was filtered out after the reaction was finished, and sulfate was calculated gravimetrically by precipitating sulfate ions as $BaSO_4$ using standard procedure[43].

According to the product analysis, sulfate recovery was 98+2% in all cases, which is consistent with Eq. (2)

$$S(IV) + 0.5O_2 \longrightarrow S(VI) \quad \ldots\ldots\ldots\ldots \quad (2)$$

RESULTS

1. Preliminary Investigation

The kinetics of both uncatalysed and CoO catalysed reaction were studies in alkaline medium in the pH range 7.5 to 8.50. In both cases, the kinetics was first order in [S(IV)] and the treatment of kinetics data is based on the determination of first order rate constant k_1 from log [S(IV)] versus time (t),plots as shown in Fig.1.

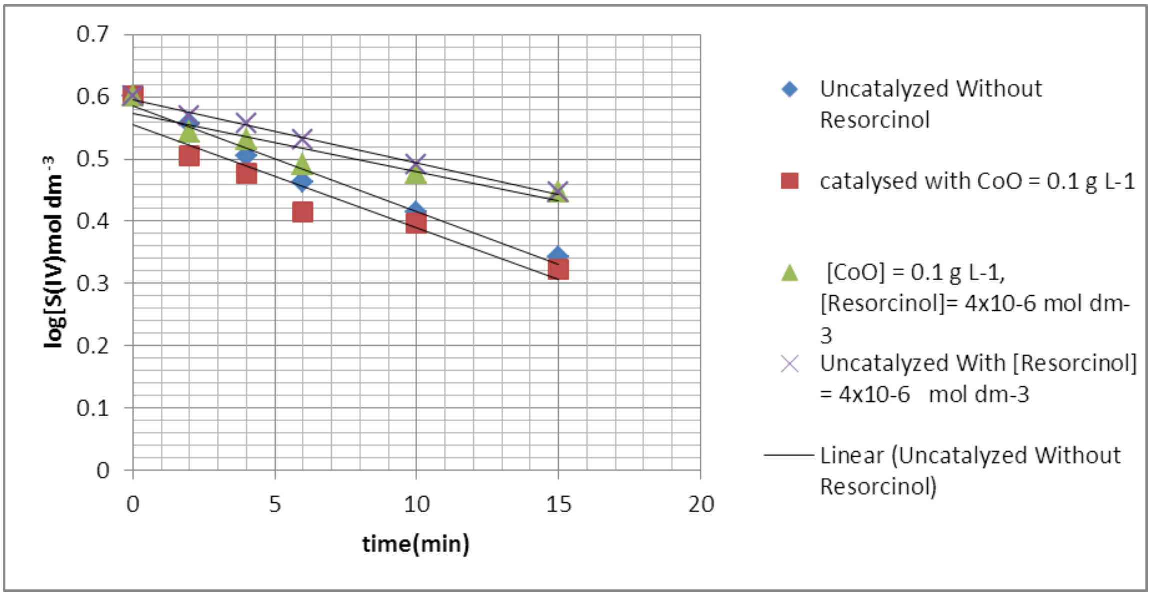

Fig.1: The disappearance of [S(IV)] with time in air-saturated suspensions at [S(IV)] = 2x10^{-3}mol dm^{-3}at Temp. = 30°C and pH = 7.50 in phosphate-buffered medium

2. Uncatalysed reaction: In ths study the reaction was studied without adding CoO.

3. Dependence of sulphite:

The detailed dependence of the reaction rate on [S(IV)] was studied by varying it is in the range 1 x 10^{-3} to 8 x 10^{-3} mol dm^{-3}at pH = 7.50, time =30°C in phosphate buffer medium.

The kinetics was found to be first order in [S(IV)] as shown in Fig.1, log [S(IV)]v/s time plots were linear. The Value of first order rate constant, k_1 are given in Table- 1, are seen to be independent of [S(IV)] and are in agreement with the rate law (3):

$-d[S(IV)]/dt = k_1[S(IV)]$……………. (3)

Table-1: **The values of k_1 for uncatalysed reaction at different [S(IV)] at pH = 7.50,Temp.= 30°C in phosphate-buffered medium**

[S(IV)]mol dm^{-3}	0.001	0.002	0.004	0.006	0.008
10^4 k_1 s^{-1}	6.837	6.496	6.332	6.706	6.117

4. [Resorcinol] dependence:

The main goal of this research was to see how different organic inhibitors affected the reaction rate of sulfur(IV) autoxidation in a phosphate-buffered medium. Resorcinol was chosen as one of the organic inhibitor compounds for this study. On increasing the concentration of resorcinol from $2x10^{-7}$ to $1x10^{-3}$ mol dm^{-3}, the rate of reaction was decreased. However, in the presence of resorcinol, the nature of the [S(IV)] dependence remained first order and did not change. The first-order rate constant k_{inh} was defined by rate law (4) in presence of resorcinol.

$-d[S(IV)]/dt = k_{inh}[S(IV)]$ ……………………………… (4)

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

Rate law (4) specified the values of first-order rate constant k_{inh} in the presence of decreasing, with rising [Resorcinol] following the rate law (5).

$k_{inh} = k_1 /(1+B[Resorcinol])$ …………… (5)

where **(B) is inhibition parameter** for rate inhibition by resorcinol.

By rearranging the equation (5) we get

$1/k_{inh} = 1/k_1 + B[Resorcinol] / k_1$ …………………… (6)

Following Eq. (6), the plot of $1/k_{inh}$ versus [Resorcinol] 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 $2.2x10^3$ s & $4.2x10^6$ mol^{-1}dm^3 s at pH =7.50, and Temp.= 30°C. The slope/intercept relationship provides us with the value of the inhibitory parameter (B), which was determined to be $1.9x10^3$ mol^{-1} dm^3.

Table-2: **The values of k_{inh} at different [Resorcinol], [S(IV)] = 2×10^{-3} mol dm^{-3},pH = 7.50, Temp. = 30°C, $Na_2HPO_4 = 8\times10^{-2}$ mol dm^{-3}, $KH_2PO_4 = 2\times10^{-2}$mol dm^{-3}**

[Resorcinol] mol dm^{-3}	$2x10^{-7}$	$5x10^{-7}$	$3x10^{-6}$	$4x10^{-6}$	$7x10^{-5}$	$2x10^{-4}$	$5x10^{-4}$	$1x10^{-3}$
10^4kinh s^{-1}	8.58	6.94	4.18	3.87	3.34	3.19	2.27	1.53
$1/k_{inh}$ s	1166	1440	2439	2591	2994	3135	4405	6536

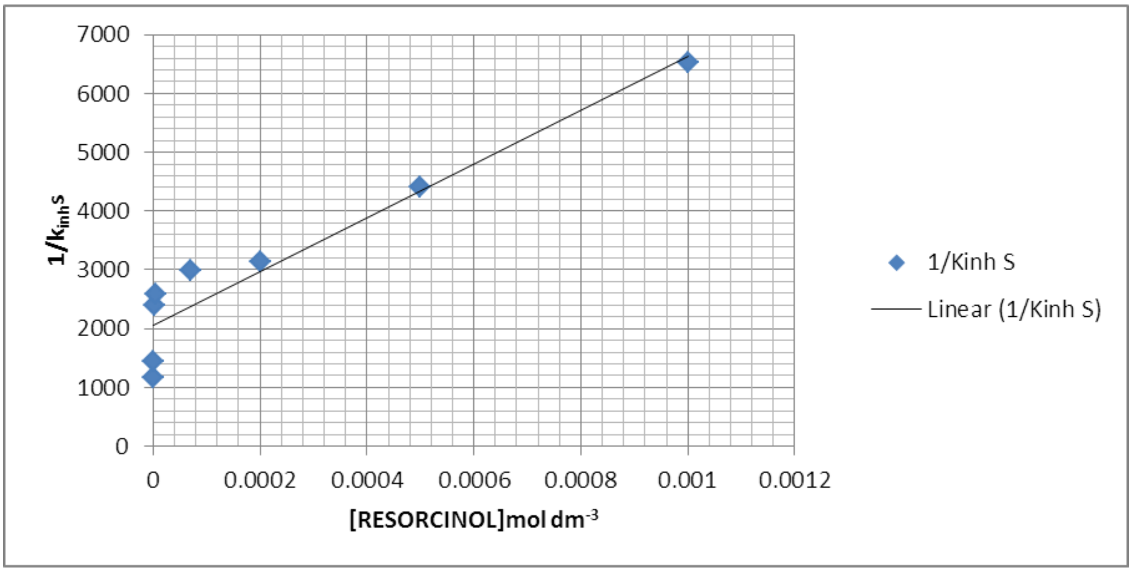

Fig.2. **Effect of Resorcinol at $[S(IV)] = 2x10^{-3}$mol dm^{-3} at Temp. = 30°C, pH = 7.50 in phosphate-buffered medium**

5. CoO - Catalysed reaction:

First of all the kinetics of CoO catalysed reaction on the autoxidation of sulfur(IV) was investigated in the absence of inhibitor-resorcinol at pH = 7.50 and Temp. = 30^oC in alkaline phosphate-buffered medium.

6. [S(IV)] variation:

[S(IV)] was varied from $1x10^{-3}$ to $10x10^{-3}$ **mol dm^{-3}** at two different but static[CoO] of 0.1 and 0.2g $L^{-1}$was carried out at pH =7.50 and time = 30^oC the results show that first order in [S(IV)] plots were linear.

7. [CoO] variation:

The effect of [CoO] was studied by varying [CoO] from 0.1g dm^{-3} to 0.5g dm^{-3} at [S(IV)] of 2×10^{-3} mol dm^{-3} at pH = 7.50 and Temp.= 30^oC in alkaline phosphate-buffered heterogeneous medium. The first-order rate constants' values k_{cat} for S(IV) autoxidation were observed at different [CoO] at pH = 7.50, Temp.= 30^oC are given in table-3.

The character of dependence of k_{cat} on [CoO] shown in fig-3 indicates the two-term rate law.

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

or

$$k_{cat} = k_1 + k_2[CoO]$$

From the graph plots in fig-3. "The values of intercept are equal to k_1 and the slope is equal to k_2 were found to be **1.5×10^{-3} s and $9.3x10^{-3}$ mol^{-1} dm^3 s,** respectively at pH = 7.50 and Temp.= 30˚C in an alkaline phosphate-buffered medium."

Table-3: **The value of k_{cat} at different [CoO] at S(IV)] = $2x10^{-3}$ mol L^{-1}, pH = 7.50, time = 30^oC**

$[CoO]g\ dm^{-3}$	0.1	0.2	0.3	0.4	0.5
$10^4 k_1\ s^{-1}$	7.07	9.87	12.30	16.11	20.33

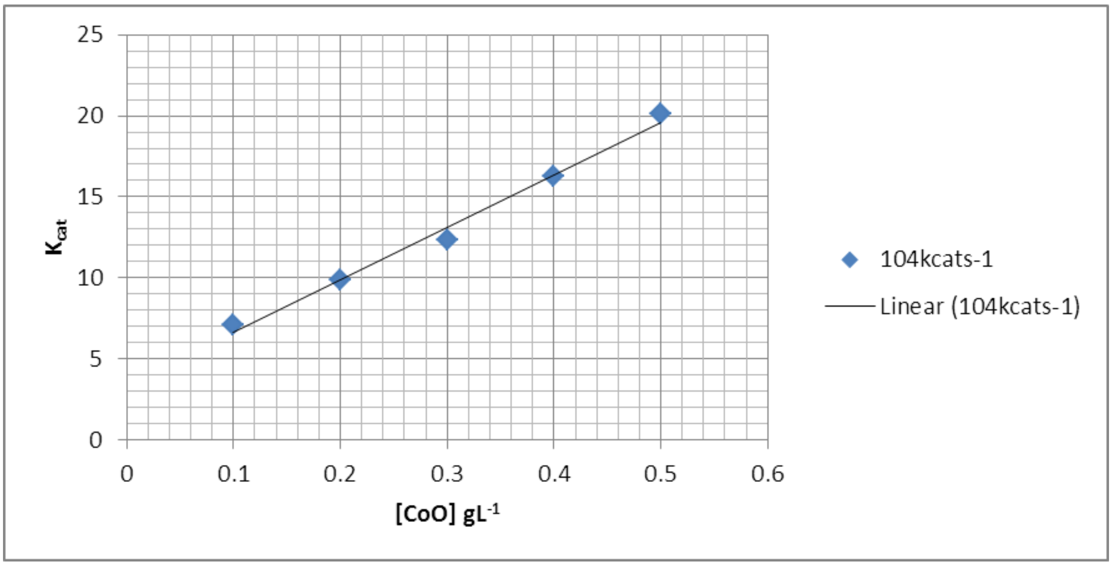

Fig. 3. Effect of CoO at [S(IV)] = 2x10^{-3}mol L^{-1}, pH=7.50 and t= 30°C, in phosphate in phosphate-buffered medium.

8. Rate of reaction studies in the presence of resorcinol:

The effect of [Resorcinol] on CoO catalysed S(IV) autoxidation [Resorcinol]variation was carried out from 2×10^{-7} to 1×10^{-3} mol dm^{-3} at two diverse [CoO] that is 0.1 and 0.2 g dm^{-3} but fixed [S(IV)] = 2×10^{-3} mol dm^{-3} at pH = 7.50 and Temp.= 30°C in alkaline phosphate-buffered medium. The results indicate that increasing the [Resorcinol] concentration decreases the rate of reaction i.e., on the other hand, inhibition happens.

In the presence of resorcinol, a comprehensive examination of the rate dependence on [S(IV)], [CoO], and pH found that the kinetics persist first order in equally [S(IV)] & [CoO] and are independent of pH. The results are given in Table-4.

A graph was plotted between [CoO] versus k_{cat} and was found linear with a non-zero intercept. **The intercept and slope values are found to be 2.9x10^{-3} s^{-1} and 4.7x10^{-3} g^{-1}dm^{3} s^{-1}.**

The dependence of observed results for the reaction follows the following rate law in presence of resorcinol. Eq.(8).

$$\frac{-d[S(IV)]}{dt} = \frac{(k_1 + k_2[CoO])\,[S(IV)]}{1 + B\,[Resorcinol]} \qquad (8)$$

$$\text{where} \quad k_{inh} = \frac{k_1 + k_2[CoO]}{1+B[Resorcinol]} = \frac{k_{cat}}{1 + B[Resorcinol]} \qquad (9)$$

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

$$\frac{1}{k_{inh}} = \frac{1}{k_{cat}} + \frac{B\,[Resorcinol]}{k_{cat}} \qquad (11)$$

By producing a second graph between $1/k_{inh}$ versus [Resorcinol], a linear line with a non-zero intercept was obtained **Fig.4.** The intercept $=1/k_{cat}$ and slope = B/k_{cat} values obtained from the graph are 2.4×10^3s and 4.4×10^6 mol^{-1} dm^3s, respectively. The value of the inhibition parameter (B) can be computed using these values: **inhibition parameter (B) = slope/intercept, which equals B = 1.83×10^3 mol^{-1} dm^3.**

Table-4.: Variation of CoO at [S(IV)] = 2×10^{-3} mol dm^{-3}, [Resorcinol] = 4×10^{-6}mol dm^{-3}, pH = 7.50, Temp.= 30°C in phosphate-buffered medium.

$[CoO](g\ L^{-1})$	0.1	0.2	0.3	0.4	0.5
$10^4\ k_{cat}s^{-1}$	3. 60	5.81	8.39	9.08	13.16

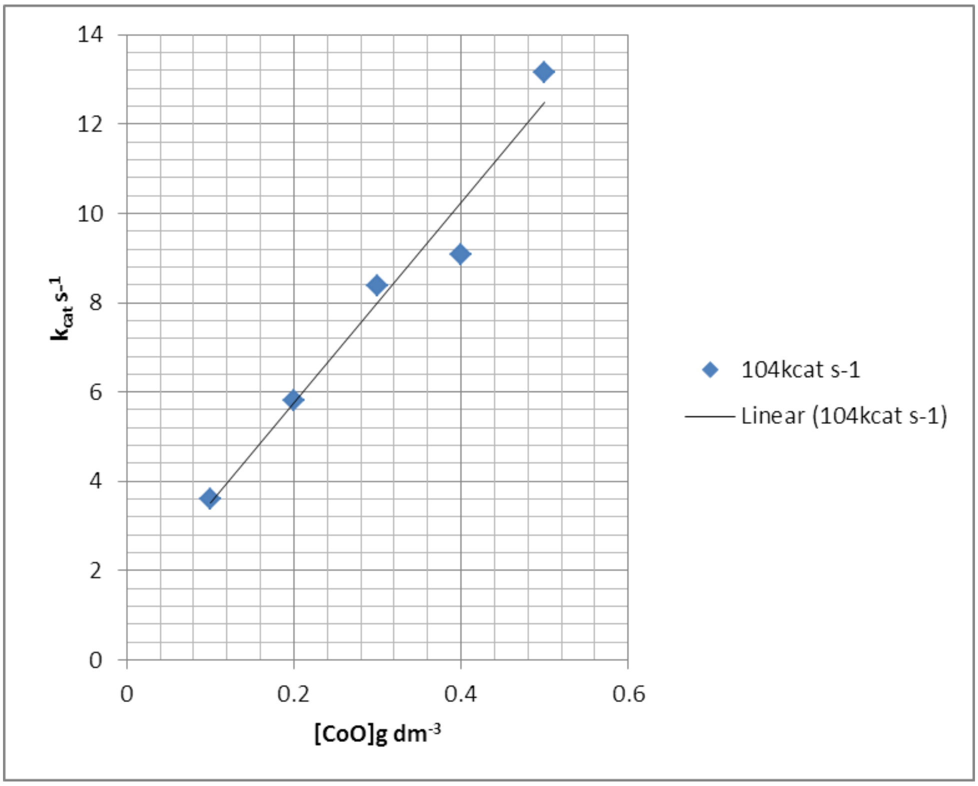

Fig. 4: Effect of [CoO] at S(IV) = $2x10^{-3}$ mol dm^{-3}, [Resorcinol] = $4x10^{-6}$ mol dm^{-3} at pH =7.50 and t = 30^{o}C in phosphate-buffered medium.

Table-5. **The variation of [Resorcinol] at [S(IV)] = 2×10^{-3}mol dm^{-3}, [CoO] = 0.1 g dm^{-3},Temp. = 30°C, pH = 7.50 in phosphate-buffered medium.**

[Resorcinol] mol dm^{-3}	$2x10^{-7}$	$5x10^{-7}$	$2x10^{-6}$	$4x10^{-6}$	$7x10^{-5}$	$2x10^{-4}$	$5x10^{-4}$	$1x10^{-3}$
$10^{-4}kinhs^{-1}$	8.47	6.79	3.73	3.60	3.20	3.01	2.16	1.47
$1/K_{inh}s$	1181	1473	2681	2778	3125	3333	4761	6803

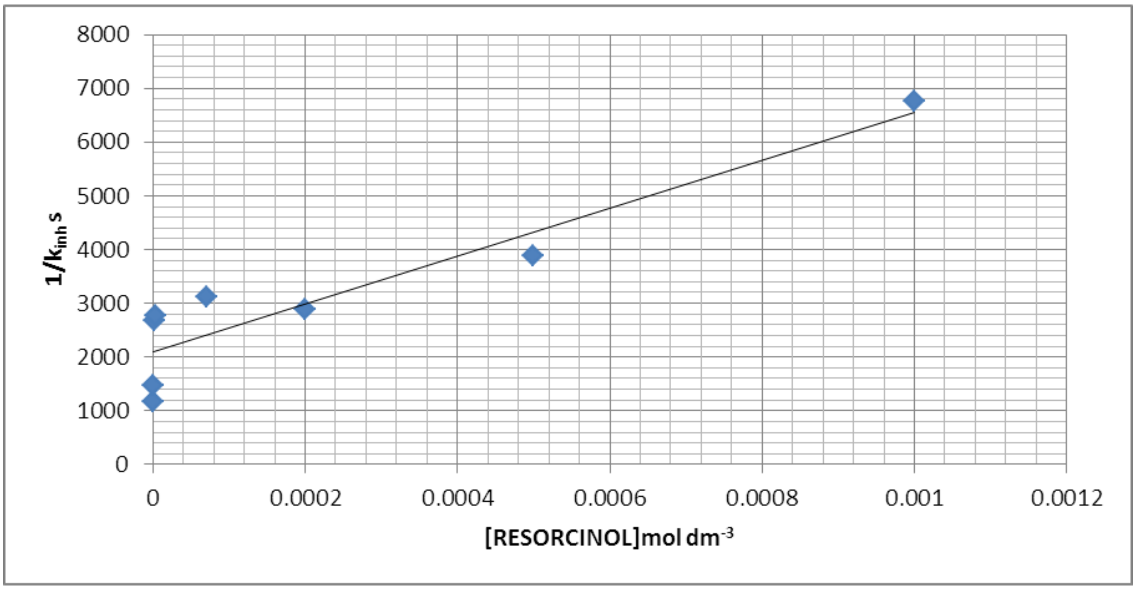

Fig. 5. Effect of [[Resorcinol] at S(IV) =2x10^{-3}mol L^{-1}, CoO= 0.1 g L^{-1}, pH =7.50, and at 30^{o}C, in phosphate buffered medium.

By producing a second graph between 1/k_{inh} versus [Resorcinol], a linear line with a non-zero intercept was obtained (fig-5)The intercept =1/k_{cat} and slope = B/k_{cat} values obtained from the graph are 2.4×10^{3}s and 4.4×10^{6} mol^{-1} dm^{3}s, respectively. The value of the inhibition parameter (B) can be computed using these values: **inhibition parameter (B) = slope/intercept, which equals B = 1.83 × 10^{3} mol^{-1} dm^{3}.**

9. Variation of pH:

Variation of pH in the range 7.50 to 8.50 in phosphate buffer medium was studied at S(IV)=2x10^{-3}, [CoO]=0.1gL^{-1}, [RESORCINOL]=4x10^{-6} at t=30^{o}C and the result show that be reaction is independent of pH. (Table.6). The effect of [buffer] was examined by varying the concentration of both Na_2HPO_4 and 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.

Table-6: **Variation of pH at [S(IV)] = 2×10^{-3} mol dm^{-3}, CoO = 0.1 g dm^{-3}, [Resorcinol] = 4×10^{-6} mol dm^{-3}, Temp. = 30°C in alkaline buffer medium**

pH	7.50	7.85	8.20	8.40
10^{4} $k_{cat}s^{-1}$	3.60	3.67	3.88	3.95

10. Effect of temperature:

k_{obs} values were determined at three distinct temperatures ranging from 30^{o}C to 40^{o}C. Table- 7,shows the results. Variation of temperature at [S(IV)] = 2×10^{-3} mol dm^{-3}, CoO = 0.1 g dm^{-3}, [Resorcinol] = 4×10^{-6} mol dm^{-3}, pH=7.50, Na_2HPO_4 = 8×10^{-2} mol dm^{-3}, KH_2PO_4 = 2×10^{-2} mol dm^{-3}

The apparent empirical energy of activation was determined to be **68.55 KJ mol^{-1}** using these measurements.

Table-7 :Effect of temperature on k_{obs} air saturated suspensions at S(IV)] = 2×10^{-3} mol dm^{-3}, [CoO] = 0.1 gdm^{-3}, [Resorcinol] = 4×10^{-6} mol dm^{-3},pH = 7.50 in phosphate-buffered medium.

Temperature (°C)	30	35	40
$10^4\, k_{obs} s^{-1}$	3.60	5.75	8.61

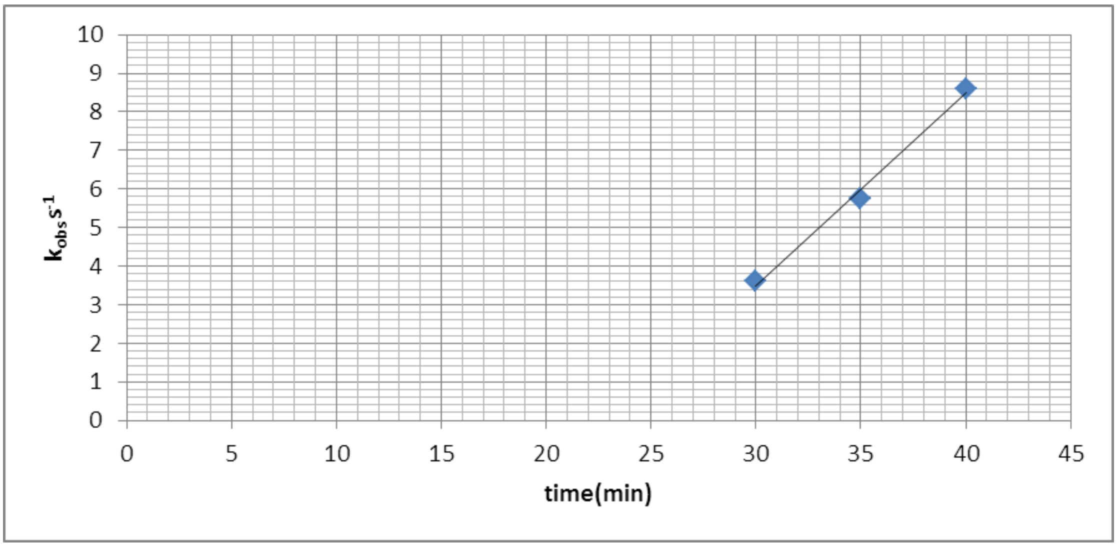

Fig.6. Effect of temperature at [S(IV)] = $2x10^{-3}$ mol dm^{-3}, [CoO] = 0.1g L^{-1},[Resorcinol] = $4x10^{-6}$mol dm^{-3},time= 30°C and pH = 7.50 .

DISCUSSION

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

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

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

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

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

K_H is Henry's and $K_{d(1)}$,$K_{d(2)}$ 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}, $K_{d(1)} = 1.4x10^{-2}$, $K_{d(2)} = 6.24x10^{-8}$ and $K_{(3)} = 7.6x10^{-2}$.

At this experiment, the SO_3^{2-} would be predominantly present in the pH range of 7.50-8.50. We have only assumed SO_3^{2-} species to be reactive in the subsequent because the rate of reaction is almost pH-independent. In several heterogeneous aqueous phase autoxidation processes of S(IV) catalysed by transition metal oxides, the formation of surficial complexes via the adsorption of S(IV) and O_2 on the particle surface and the oxidation of S(IV) via the participation of multiple oxidation states have been postulated.

The dependence of oxygen in the current investigation reveals that the creation of surficial complex by adsorption of O_2 on the particle surface of CoO occurs in a quick step.

The addition of resorcinol, like ethanol, slows down the rate of catalysed reactions of CoO in alkaline media, according to Gupta *et al.,* (1991)[44]. This suggests the presence of oxy sulphur free radicals such as SO_3^-, SO_4^-, and SO_5^- in a radical mechanism. The inhibition is produced by inhibitors that scavenge SO_4^-, such as benzene and ethanol.

According to Begum *et al.*, (2018)[45] a radical mechanism is at work in reactions when the inhibition value is between 10^3-10^5. The value of the inhibitory parameter-B was determined to be $1.83\text{x}10^3$ mol^{-1} dm^3 in this investigation, which is within the same range. In the presence of resorcinol, this strongly agreed with the radical mechanism for the CoO–catalysed reaction.

Based on findings, including resorcinol, the following radical mechanism is hypothesized, which is similar to that described by Gupta *et al.,* (1999), Sameena *et al.,* (2018)[45] and Mudgal *et al.,*(2008)[48] in the ethanol inhibition of the CoO catalysed reaction.

$$\text{CoO} + SO_3^{2-} \xrightleftharpoons{K_1} \text{CoO}.SO_3^{2-} \ldots\ldots\ldots\ldots \tag{16}$$

$$\text{CoO}.SO_3^{2-} + O_2 \xrightleftharpoons{K_2} \text{CoO}.SO_3^{2-}.O_2 \ldots\ldots\ldots \tag{17}$$

$$\text{CoO}.SO_3^{2-}.O_2 \xrightarrow{k_1} \text{CoO} + SO_3^{-\bullet} + O_2^{-} \ldots \tag{18}$$

$$SO_3^{-\bullet} + O_2 \xrightarrow{k_2} SO_5^{-\bullet} \ldots\ldots\ldots\ldots\ldots\ldots \tag{19}$$

$$SO_5^{-\bullet} + SO_3^{2-} \xrightarrow{k_3} SO_5^{2-} + SO_3^{-\bullet} \ldots\ldots\ldots\ldots \tag{20}$$

$$SO_5^{-\bullet} + SO_3^{2-} \xrightarrow{k_4} SO_4^{-\bullet-} + SO_4^{2-} \ldots\ldots\ldots\ldots \tag{21}$$

$$SO_5^{2-} + SO_3^{2-} \xrightarrow{k_5} 2SO_4^{2-} \ldots\ldots\ldots\ldots \tag{22}$$

$$SO_4^{-\bullet} + SO_3^{2-} \xrightarrow{k_6} SO_4^{2-} + SO_3^{-\bullet} \ldots\ldots\ldots \tag{23}$$

$$SO_4^{-\bullet} + X \xrightarrow{k_7} \text{Nonchain product} \ldots\ldots\ldots\ldots\ldots\ldots \tag{24}$$

$$SO_4^{-\bullet} + \text{Resorcinol} \xrightarrow{k_8} \text{Nonchain product} \ldots \tag{25}$$

O_2^-, which is likewise known to react slowly with sulphur (IV), has no part in the mechanism. It may disproportionately create H_2O_2 and O_2 or impurities may scavenge it. By setting $d[SO_3^-]/dt$, $d[SO_4^-]/dt$, and $[SO_5^-]$/dt to zero and assuming the steady-state approximation and long-chain hypothesis. The rate of commencement can be shown to be equal to the termination rate.

$k_1[CoO(SO_3^{2-})(O_2)] = \{k_7[X] + k_8[Resorcinol]\}[SO_4^{\cdot-}]$ (26)

Since the reaction is entirely stopped in the existence of Resorcinol at $1x10^{-3}$ mol dm^{-3}, the steps (18) and (22) appear to be unimportant. The contribution of propagation reaction (Eq. 21) plays a significant role in the CoO catalyzed reaction. The reaction is halted in the occurrence of a large amount of Resorcinol concentration, even though the autoxidation reaction should have occurred even in the occurrence of a high Resorcinol amount. As a result, we decided to disregard the step (Eq. 21) and merely assume the reaction rate indicated by the 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

$$R_{cat} = \frac{k_6\ k_1\ [CoO\ .SO_3^{2-}.O_2][SO_3^{2-}]}{k_7[X] + k_8\ [Resorcinol]} \qquad (28)$$

From equilibrium Eq.13 and Eq.14

$$R_{cat} = \frac{k_6\ K_1K_2\ [CoO][S(IV)][O_2]}{\{1+k_1[S(IV)]k_7[X] + k_8\ [Resorcinol]\}} \qquad (29)$$

At fixed O_2, replacing $k_6\ K_1\ K_2[O_2]$ by k^1 we get

$$R_{cat} = \frac{k^1\ [CoO][S(IV)]}{\{1+k_1[S(IV)]k_7[X] + k_8\ [Resorcinol]\}} \qquad (30)$$

Since we observed that reaction rate clear first order in [S(IV)], The value of $k_1[S(IV)] << 1$ so the above rate law can be reduced to

$$R_{cat} = \frac{k^1\ [CoO][S(IV)]}{k_7[X] + k_8\ [Resorcinol]\}} \qquad (31)$$

The inhibition constant-B has been calculated to be $1.83x10^3$ $mol^{-1}dm^3$. As a result, it's concluded that resorcinol serves as a free radical scavenger in the CoO-catalysed autoxidation of aqueous sulfur dioxide in an alkaline medium and that a free radical mechanism is at work in this system[47,48].

CONCLUSION

Resorcinol was reported to act as an inhibitor in CoO catalysed SO_2 autoxidation in an alkaline medium, and a free radical mechanism was hypothesized based on the observed rate law.

$-d[S(IV)]/dt = (k_1+k_2[CoO])[S(IV)]/1 + [Resorcinol]$

The rate constants and order of the reactions were determined using the experimental data. The reaction order in SO_2 was first-order in both the presence and absence of resorcinol. The influence of pH on SO_2 oxidation was tested in the presence of CoO and resorcinol, and it was observed that the rate of SO_2 oxidation was independent of the pH change during the process. The apparent empirical energy of activation for the reaction is **68.55 KJ mol^{-1}** when a graph of log k v/s 1/T is plotted. Our findings suggest that the resorcinol used in this study turns as an inhibitor rather than a catalyst for SO_2 autoxidation.

The inhibition factors (B) for uncatalysed and CoO catalysed autoxidation of SO_2 in the existence of resorcinol are 1.9×10^3 mol^{-1} dm^3 and 1.83×10^3 mol^{-1} dm^3, respectively, which are consistent with previous findings of inhibition factors in the 10^3-10^5 range.

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