CO$_2$O$_3$CATALYSED AUTOXIDATION OF SULPHUR DIOXIDE AND INHIBITION BY RESORCINOL

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ABSTRACT

Like many other organic compounds, the aromatic and aliphatic alcohols are present in the atmosphere and therefore, looking to their possible affects autoxidation of S (IV). So following rate law has been proposed based on the observed results.

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

KEYWORDS: *Co$_2$O$_3$; Catalysis; Inhibition; Resorcinol; S (IV); Acid Rain*

INTRODUCTION

Various studies have been done on the atmospheric oxidation of S (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 SO$_2$ in to acid sulfate. The reviews by Huie and peterson[1], Hoffmann and Boyce[2], Hoffmann and Jacob[3] deal with the oxidation of S (IV) by transition metal ions and their role in catalyzing the dioxide-S(IV) systems. The metalxides, which are present in the Atmosphere are integral part of suspended particulate matter. The role of various metal oxides such as CoO[4]; Co$_2$O$_3$[5]; Ni$_2$O$_3$[6]; CuO[7]; MnO$_2$[8]; and Cu$_2$O[9]; and MnO$_2$[10] in acidic medium has been studied and given a two term rate law.Gupta[11] et al studied the inhibiting effect of alcohol on the CoO, Co$_2$O$_3$ and Ni$_2$O$_3$catalysed autoxidation reaction in alkaline medium and proposed a radical mechanism. The effect of alcohols has been studied on several catalysed S(IV) autoxidation in the effect of silver (I) catalyzed autoxidation of S(IV) in acetate buffer medium.[11-12] To explain these results and inhibition effect of organic compounds, the radical mechanism involving SO$_3$, SO$_4$ and SO$_5$ radicals was proposed.[13] Further experiments were conducted for finding reactivity of oxysulphur radicals with organics, which proved that these compounds react with SO$_4$ The reactions with SO3 and SO$_5$ appeared to be quite slow and hence unimportant. These studies have shown the reaction of SO$_4$ to be very fast.[14]Connick and Zhang[15] reported that the inhibition effect of methanol on autoxidation of S (IV) in the presence of Mn(II) ions is complex and in which sulfate radicals are scavenged. So far, inhibiting effect of resorcinol on the metal oxide catalysed autoxidation of aqueous sulfur dioxide is not studied. So in view of the knowing the inhibiting effect of resorcinol on the Co$_2$O$_3$catalysed autoxidation of sulfur dioxide in the alkaline medium the present study is under taken

Experimental

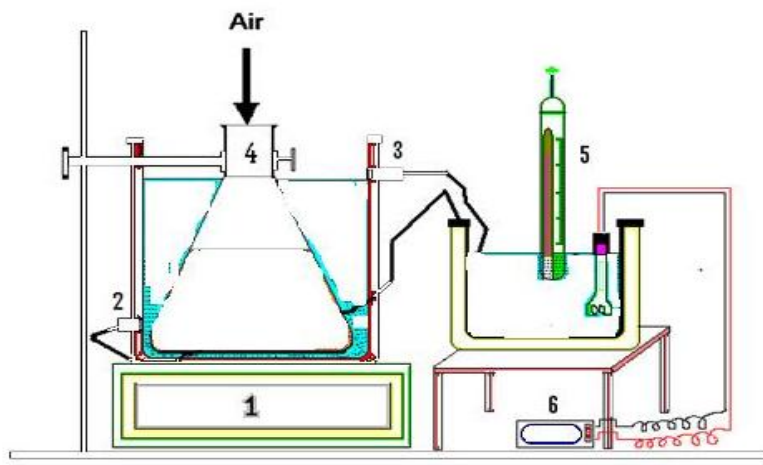The schematic representation of experimental procedure is shown in following scheme[16]

Figure 1: 1. Magnetic Stirrer, 2. Water Inlet, 3. Water Outlet, 4. Erlenmeyer Flask, 5. Thermometer, 6. Thermostat.

Product Analysis

The Recovery of sulfate[16] to be 98 ± 2 % in agreement with Equation.1.

$$S(IV) \; + \; 0.5 \; O_2 \; \rightarrow \; S(VI)$$

(1)

RESULTS

Preliminary Investigation

By plotting a graph between log [S(IV)] versus time, t we observed a straight line which confirm that reaction is followed first order kinetics (Figure 2).

Unanalyzed Reaction

In this study, the reaction was studied without adding Co_2O_3.[17].

[S(IV)] Dependence

The dependence of reaction rate on [S(IV)] follows the following rate law by observed results of Table-1.

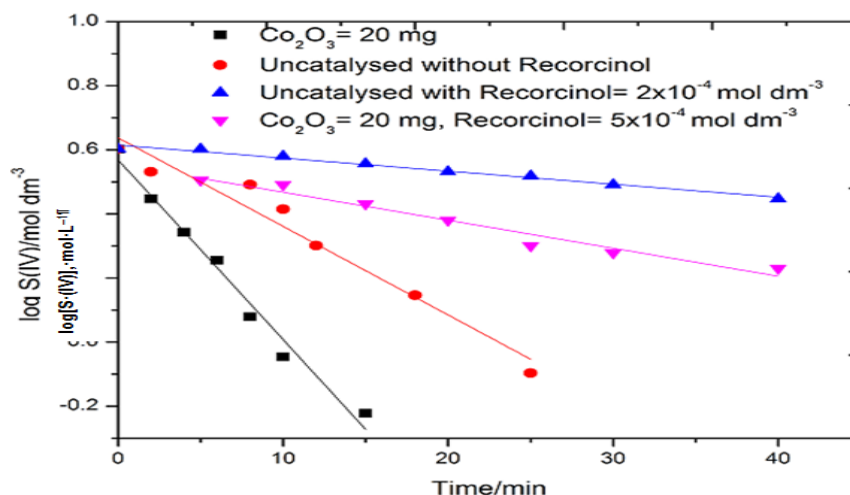$$-d \, [S(IV)] \, /dt = k_1 \, [S(IV)]$$

(2)

Figure 2: 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.

Table 1: The Values of K_1 for Unanalyzed Reaction at Different [S(IV)] at Ph= 7.40 and T = 30^0C

[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

[Resorcinol] dependence

On varying the [resorcinol] from 0.5×10^{-3} to 4×10^{-3} mol L^{-1}, the rate of the reaction becomes decelerated (Table 2). The k_{inh} in the presence of resorcinol was defined by the following rate law[18] (3)

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

(3)

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

(4)

$$1/k_{inh} = 1/k_1 + B\,[Resorcinol]/k_1$$

(5)

From Equation (5) we plot a graph between $1/k_{inh}$ versus [resorcinol] was found linear fig. 2 Where intercept = 2.79×10^3 s and slope = 3.83×10^6 mol^{-1}L B= 1.37×10^3 mol^{-1} L.at pH = 7.40, and t=30ºC.

Table 2: The Value of K_{inh} At [S(IV)] = 2 X 10^{-3} Mol L^{-1}, Ph= 7.40, T = 30°C

[Resorcinol]	K_{inh}	$1/K_{inh}$
0	6.19×10^{-4}	1616
1×10^{-4}	2.54×10^{-4}	3937
2×10^{-4}	1.97×10^{-4}	5076
3×10^{-4}	1.48×10^{-4}	6757
4×10^{-4}	1.02×10^{-4}	9804
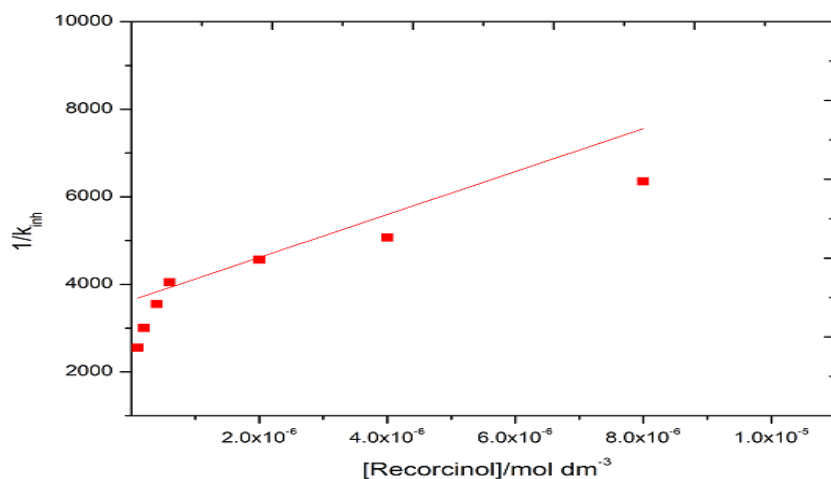
Figure 3: Effect of Resorcinol at [S(IV)] = 2 × 10^{-3}mol L^{-1}, Ph = 7.40 and at 30°C, in Alkaline Medium.

[Co$_2$O$_3$] Variation

The values of $k_{cat,}$ for S(IV) - autoxidation was determined at different [Co$_2$O$_3$] are given in Table 3.

The k_{cat} depends on [Co$_2$O$_3$] shown in Fig 3 also follows a two term rate law[19]

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

$$k_{cat} = k_1+k_2 [Co_2O_3] \tag{7}$$

Table 3 - The Value of Kcat at Different [Co2O3] at Ph = 7.40 and T = 30ºc

Co2O3(G L-1)	103kcat S-1
0.1	8.8
0.2	13.7
0.3	16.9
0.4	21.8
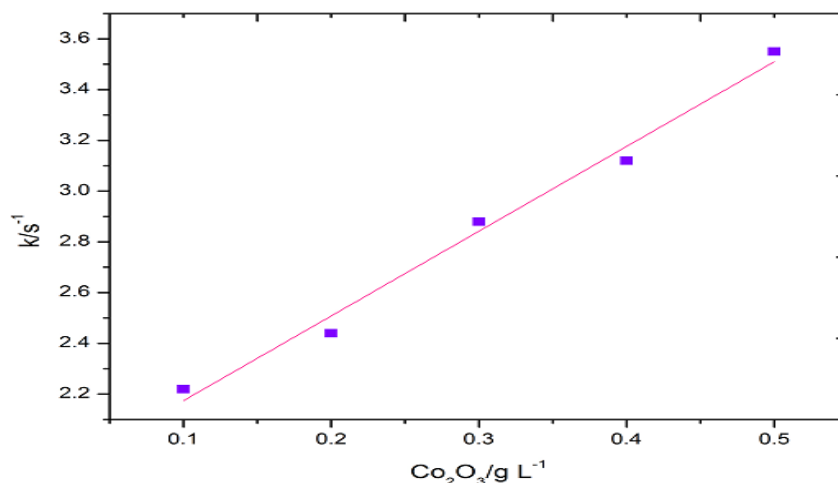
Figure 4: The Dependence of Rate on Catalyst Concentration at [S(IV)] = 2×10^{-3}mol L^{-1}, at T=30°C and Ph = 7.40 Intercept =5.1 × 10^{-4} S Slope= 4.01 × 10^{-3} Mol^{-1} L S,

Variation of pH

Variation in pH (7.40 to 8.80) in alkaline buffer medium showed the rate of reaction is independent[20] to pH (Table 4).

Table 4: Variation of Ph at $[Co_2O_3]$ = 0.2 G L^{-1}, [Resorcinol] =.5×10^{-3}mol L^{-1} [S(IV) = 2×10^{-3}mol L^{-1} and T = 30ºc

$[S(IV)]Mol l^{-1}$	$[Co_2O_3]$ G L^{-1}	[Resorcinol] $Mol l^{-1}$	Ph	Temperature, Oc	$10^4 k_{cat} K_1 + K_2[Co_2O_3]$
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 resorcinol in presence of Co_2O_3

The results indicates that by increasing the [resorcinol], the rate tend to decreases in the presence of Co_2O_3. (Figure 5)

A graph has been plotted between $[Co_2O_3]$ v/s k_{cat} found linear so follows first order kinetics[21]. The reaction follows the following rate law[20] in the presence of resorcinol (Figure 6)

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

$$k_{inh} = (k_1 + k_2[Co_2O_3] / 1 + B[Resorcinol] = k_{cat} / 1 + B[Resorcinol] \tag{9}$$

$$1/ k_{inh} = 1 + B[Resorcinol] / k_{cat} \tag{10}$$

$$1/ k_{inh} = 1/k_{cat} + B[Resorcinol] / k_{cat} \tag{11}$$

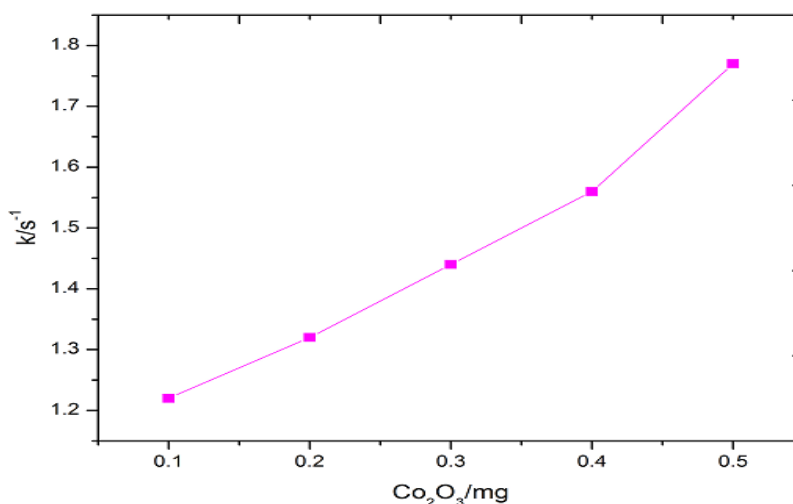
Figure 5: Effect of [S(Lv)] at Resorcinol = 2×10^{-4} G L^{-1}, Ph=7.90 and at 30°C, in Phosphate Buffered Medium Intercept and Slope are Found to be 3.67 × 10^{-5} S^{-1} and 2.78 × 10^{-5} G^{-1} L S^{-1} Respectively.
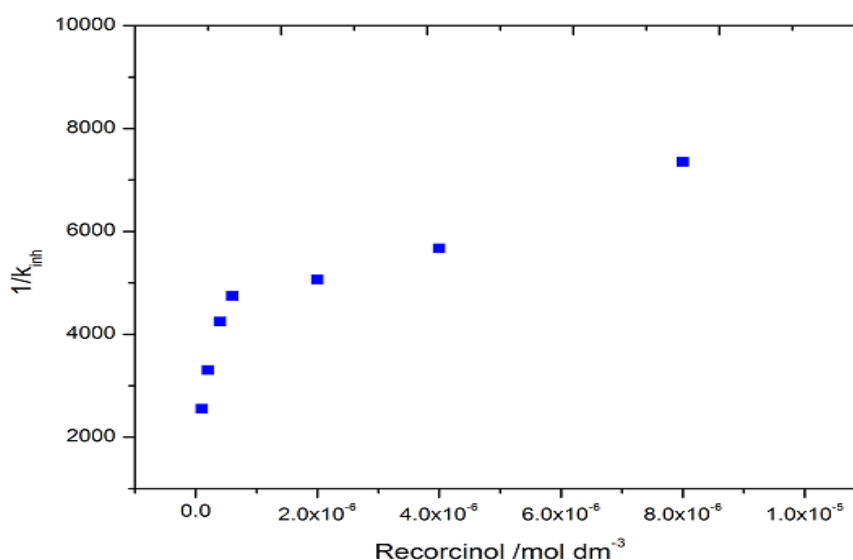
Figure 6: plot of $1/K_{inh}$v/S [Resorcinol] at [S(IV)] = 2×10^{-3} Mol L^{-1}, T = 30°C, [Co_2O_3] = 10mg, and Ph = 7.90 in Phosphate Buffered Medium Intercept = 2.40×10^3 S, Slope = 1.68×10^6 mol^{-1} L S B= = 0.70×10^3 Mol^{-1} L.

Effect of temperature

The effect of temperature on SO_2 oxidation in the presence of resorcinol and Co_2O_3 is given in table-5 and it is observed that rate of reaction increases by rising the temperature. So from these data, apparent energy[22] of activation determined and found 26. 12 kJ mol^{-1}.

Table 5: Effect of Temperature at [S(IV)] = 2×10^{-3} mol L^{-1}, [Co_2O_3] = 0.2 G L^{-1}, [Resorcinol] = $.5 \times 10^{-3}$ mol L^{-1}, T = 30°C, and Ph = 7.40

T °C	10^4 K_{obs}, S^{-1}
30	5.02
35	7.47
40	9.45

DISCUSSIONS

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[23].

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

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

$$HSO_3^- \xrightleftharpoons{K_2} SO_3^- + H^+ \tag{14}$$

$$2HSO_3^- \xrightleftharpoons{K_3} S_2O_5^{-2} + H_2O \tag{15}$$

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}, $K_1=1.4\times10^{-2}$, $K_2=6.24\times10^{-8}$, 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[24]. Grgic*et al.*(1998, 1999)[25-26]; Wolf *et al.* (2000)[27] 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[28] 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*[29] found that acetate and formate ions shows substance inhibiting effect at pH $\geq$ 5 but negligible inhibition at pH $\leq$ 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[30].

In alkaline medium the rate of Co_2O_3 catalysed reaction is highly decelerated by the addition of resorcinol 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.[31]

As reported by Gupta et al[32] 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 – catalyzed reaction in presence of resorcinol. Based on the observed results including the inhibition by resorcinol, the following radical mechanism is proposed which similar to that proposed by Gupta et al in the ethanol inhibition of the CoO catalyzed reaction.

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

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

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

$$SO_3^{-1} + O_2 \xrightarrow{k_2} SO_5 \tag{19}$$

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

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

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

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

$$SO_4 + x \xrightarrow{k_7} \text{Non Chain product} \tag{24}$$

$$SO_4 + \text{Resorcinol} \xrightarrow{k_8} \text{Non Chain product} \tag{25}$$

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

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

Since the reaction is completely stopped in the presence of [resorcinol] 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 presence of high resorcinol concentration. But this is not true and the reaction is completed seized in the presence of high concentration of resorcinol. This led us to ignore the step (18) and assume only the rate of reaction given by equation (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 reduced to

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

Gupta et al and Sharma et al proposed a similar mechanism for the CoO catalyzed 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 1.12×10^4 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 resorcinol act as a free radical scavenger in the Co_2O_3 catalyzed autoidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system.

CONCLUSIONS

The role of resorcinol act 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.

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

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 resorcinol.

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.

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Conflict of Interest: Nil

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