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Effect of Isopropyl Alcohol on Autoxidation of S (IV) Catalyzed by Co_2O_3 in Alkaline Medium

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Abstract

The kinetics of the iso propyl alcohol inhibited Co_2O_3 catalysed autoxidation of sulfur (IV) in alkaline medium has been studied and based on the observed results rate law and a free radical mechanism has been proposed.

$$\frac{-d[S(lV)]}{dt} - \frac{(k_1 + k_2[Co_2O_3])\,[S(lV)]}{1 + B\,[IPA]^*}$$

*IPA = iso propyl alcohol

Keywords: Kinetics; Autoxidation; SO_2; Co_2O_3; Catalysis; Inhibition; Iso propyl alcohol

1. INTRODUCTION

The atmospheric oxidation of sulfur (IV) in the recent past and large number of studies carried out in aerosols and in bulk aqueous phase. The trace metal ions which are part of all atmospheric systems and are catalysing the oxidation of aqueous sulfur dioxide in to acid sulphate. The reviews by Huie and Peterson [1], Hoffmann and Boyce [2], Hoffmann and Jacob [3] deal with the oxidation of sulfur(IV) by transition metal ions and their role in catalysing the dioxygen-S(IV) systems. The metal oxides, which are released to the atmosphere as a result of combustion processes are integral part of suspended particulate matter. The catalytic role of several metal oxides such as CoO [4]; Co_2O_3 [5]; Ni_2O_3 [6]; CuO [7]; MnO_2 [8]; and Cu_2O [9]; Ag [10] in acidic medium has been studied and given a two term rate law.

Gupta [10] et al studied the inhibiting effect of alcohol on the CoO, Co_2O_3 and Ni_2O_3 catalysed autoxidation reaction in alkaline medium and proposed a radical mechanism for CoO and Co_2O_3. Biglow [12] (1898) was first to report that, alcohols slow down the reaction between sodium sulphite and oxygen. Aleya and Back strom [13] studied the inhibiting effect of aliphatic alcohols such as ethanol, iso propanol, secondary butanol and benzyl alcohol on the oxidation of sodium sulphite in alkaline conditions.

Connick and Zhang [14] reported that the inhibition effect of methanol on autoxidation of sulfur(IV) in the presence of Mn(II) ions is complex and in which sulphate radicals are scavenged. Sharma *et al* [15-17] reported organic compunds inhibited S(IV) oxidation by Ag (I) in acidic medium.

So far inhibiting effect of iso propyl alcohol on the metal oxide catalysed autoxidation of aqueous sulfur dioxide is not studied. So in view of the knowing the inhibiting effect of iso propyl alcohol on the Co_2O_3 catalysed autoxidation of sulfur dioxide in the alkaline medium the present study is under taken.

2. EXPERIMENTAL

The experimental procedure was exactly the same as described earlier [18-19] 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, $30.\pm 0.1^0$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 $100m^3$) for obtaining the desired pH. The kinetics were followed 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 generally better than ± 10%. All calculations were performed in MS Excel.

3. PRODUCT ANALYSIS

The qualitative tests showed sulphate 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 sulphur (IV). When the reaction was complete, Co_2O_3 was filtered out and sulphate was estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure [20, 21].

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

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

4. RESULTS

4.1 Preliminary Investigation

The kinetics of both uncatalyzed and Co_2O_3 catalyzed reaction were studied in alkaline medium in the pH range 7.3-8.8. 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.

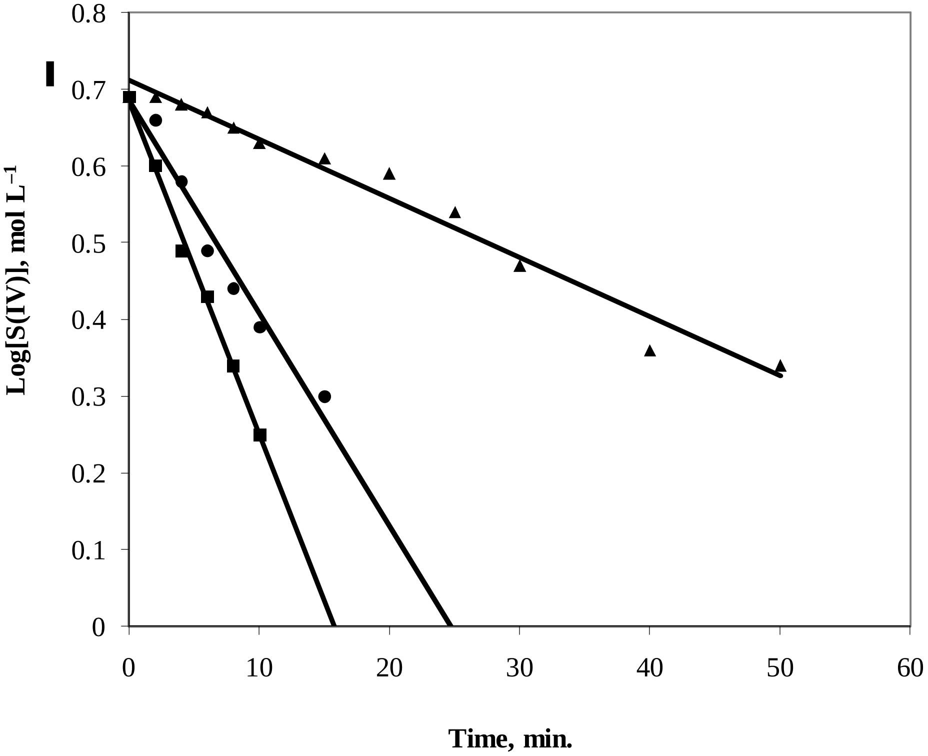

Fig. 1: The disapperance of [S(IV)] with time in air - saturated suspensions at [S(IV)] = 2×10^{-3} mol L^{-1},at 30° C and pH = 7.34, (■)Co_2O_3 = 20 mg,IPA. = 0 ml,(●) Co_2O_3 = 0mg, IPA = 0 ml,(▲) = Co_2O_3 = 20mg , IPA = 7.8×10^{-4},

4.2 Uncatalysed Reaction

This study was done in the absence of catalyst.

4.3 Dependence of Sulphite

The detailed dependence of the reaction rate on [S(IV)] was studied by varying it is in the range 1×10^{-3} mol dm^{-3} to 6×10^{-3} mol dm^{-3} at pH= 7.34 , t = 30°C in phosphate buffer medium. The kinetics was found to be pseudo 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)] in agreement with the rate law (2).

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

Table 1: The values of k_1 for uncatalysed reaction at different [S(IV)] atpH= 7.34 and t = 30^0C

[S(IV)] mol dm^{-3}	**$10^4 k_1\ s^{-1}$**
0.001	10.5
0.002	10.6
0.004	10.1
0.006	10.5

4.4 Iso propyl alcohol] dependence

The major aim of this study was to examine the effect of organic inhibitors on the reaction rate, iso propyl alcohol was chosen as this study. On increasing the concentration of iso propyl alcohol from 1.04×10^{-4} to 1.56×10^{-3} mol L^{-1}, the rate of reaction decreased.However, the nature of the [S(IV)] – dependence in presence of iso propyl alcohol did not change and remained first order. The first order rate constant k_{inh}, were defined by rate law (3)

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

The values of k_{inh} decreased with increase in iso propyl alcohol in agreement with the rate law.

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

where B is inhibition parameter for rate inhibition by iso propyl alcohol.
The equation (4) on rearrangement becomes

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

In accordance with eq. (5) the plot of $1/k_{inh}$ versus [IPA] was found to be linear with a non-zero intercept, (Fig. 2). The values of intercepts($1/k_1$) and slope (B/k_1) were found to be **1.29×10^3 s** and **6.4×10^6 mol^{-1} Ls** at pH = 7.34, and 30ºC.From these values the value of inhibition parameter B was found to be, **4.9×10^3 $mol^{-1}L$.**

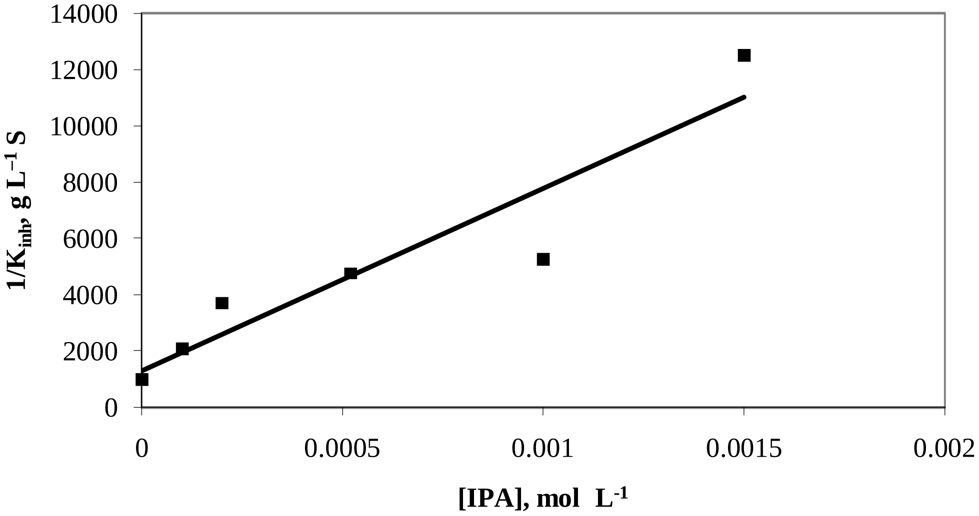

Fig. 2: Effect of IPA at [S(IV)] = 2×10^{-3} mol L^{-1}, pH = 7.34 and at 30°C, in phosphate buffered medium

4.5 Co_2O_3 -Catalyzed Reaction

At first the kinetics of Co_2O_3-catalyzed reaction in the absence of IPA was studied.

4.6 [S(IV)] Variation

The concentration of S(IV) was varied from 1×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3}at two different but fixed [Co_2O_3] of 0.1 and 0.2 g L^{-1} was carried out at pH = 7.34 and t=30°C. The kinetics was found to pseudo- first order in both cases.

4.7 [Co_2O_3] Variation

The effect of [Co_2O_3] on the rate was studied and the values of first order rate constants $k_{cat,}$ for S(IV) - autoxidation was determined at different [Co_2O_3] at pH=7.34, t=30°C. The results are given in Table 2.

Table 2: The value of k_{cat} at different $[Co_2O_3]$ at pH = 7.80 and t = 30ºC

$Co_2O_3 (g\ L^{-1})$	**$10^3 k_{cat}\ s^{-1}$**
0.1	8.8
0.2	13.7
0.3	16.9
0.4	21.8

It follows a rate law given by (6)

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

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

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} dm^{-3} s

4.8 Variation of pH

Variation in pH in the range 7.4 to 8.8 in phosphate buffer medium showed the rate to be independent of pH. The results are given in Table 3. 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 tables. The values showed that the rate of the reaction to be insensitive to the buffer concentration in Table 3.

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

$[S(IV)] mol L^{-1}$	**$[Co_2O_3]$ $g\ L^{-1}$**	**[Aniline] $mol L^{-1}$**	**pH**	**Temp.**	**$10^4 k_{cat}$ $k_1 + k_2[Co_2O_3]$**
0.002	0.2	0.000156 M	7.40	30°C	7.6
0.002	0.2	0.000156 M	7.80	30°C	7.75
0.002	0.2	0.000156 M	8.10	30°C	7.51
0.002	0.2	0.000156 M	8.80	30°C	7.79

Rate Law in the Presence of iso propyl alcohol

A detailed study of dependence of rate on [S(IV)] , $[Co_2O_3]$, and pH on the reaction in the presence of iso propyl alcohol revealed that the kinetics remain first order both in [S(IV)] and $[Co_2O_3]$ and independent of pH in agreement with the following rate law.

$$\frac{-d[S(lV)]}{dt} = \frac{(k_1+ k_2[Co_2O_3])\ [S(lV)]}{1 + B\,[IPA]} \qquad (8)$$

where $$k_{inh} = \frac{k_1+ k_2[Co_2O_3])}{1 + B\,[IPA]} = \frac{k_{cat}}{1 + B\,[IPA]} \qquad (9)$$

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

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

A plot between $[Co_2O_3]$ v/s first order rate constant is linear fig. 3 with intercept **$4.2 \times 10^{-4} s^{-1}$** and slope **$1.2 \times 10^{-3}$ g^{-1} L s^{-1}**.

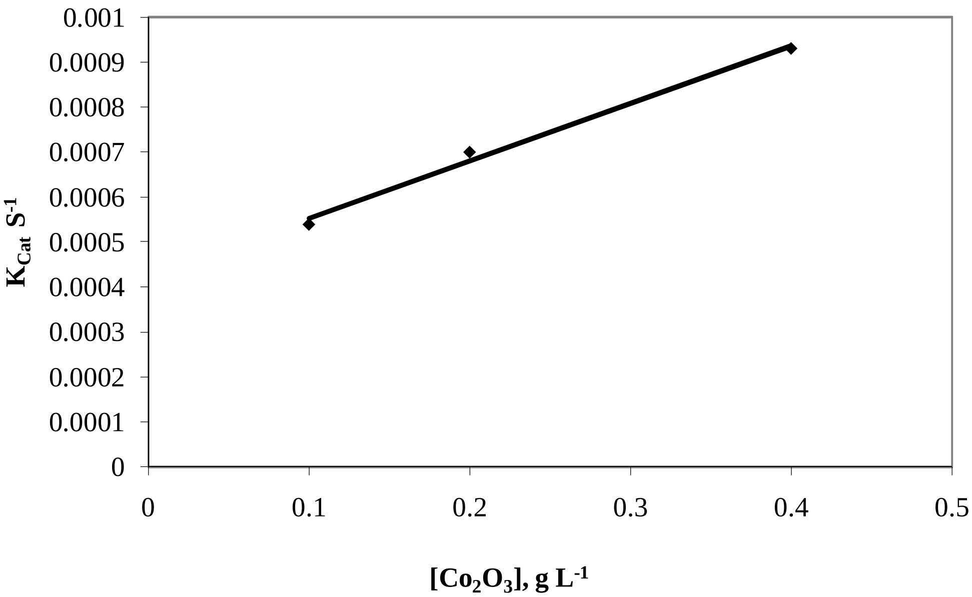

Fig. 3: Effect of [S(lV)] at IPA = 1.56×10^{-4} g L^{-1} , pH=7.34 and at 30°C, in phosphate buffered medium.

Table 4 The variation of [IPA] at[S(IV)] = 2×10^{-3} mol L^{-1}, $[Co_2O_3]$ = 0.1 g L^{-1}, t = 30°C, and pH = 7.80.

[IPA]	**K_{inh} s^{-1}**	**$1/K_{inh}$ s**
0	10.1×10^{-3}	990
1×10^{-3}	5.0×10^{-3}	2000
2×10^{-3}	3.8×10^{-3}	2631
5×10^{-3}	2.7×10^{-3}	3704
5.2×10^{-3}	0.8×10^{-3}	12500

A plot between $1/K_{inh}$ vs [aniline] is linear fig. 6.5, with intercept = **3.86×10^2 s** and slope = **$1.49 \times10^6 mol^{-1}$ L s** from which the value of **B = $3.8 \times 10^3 mol^{-1}$ L**.

4.10 Effect of temperature

The values of k_{obs} were determined at three different temperatures in the range 30°C to 40°C. The results given in Table 5. These values yielded an apparent empirical energy of activation 16.44 kJ mol^{-1}.

Table 5: Effect of temperature on k_{obs} air saturated suspensions at

[S(IV)] = 2×10^{-3} mol L^{-1}, $[Co_2O_3]$ = 0.2 g L^{-1}, [IPA] =1.56×10^{-4} mol L^{-1},t = 30°C, and pH = 7.40.

T°C	**10^4 k_{obs},s^{-1}**
30	7.59
35	10.0
40	11.50

5. DISCUSSION

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

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

$$SO_2.H_2O\,(aq.) \overset{K_1}{\rightleftharpoons} HSO_3^{-1} + H^+ \qquad (13)$$

$$HSO_3^{-1} \overset{K_2}{\rightleftharpoons} H^+ + SO_3^{-2} \qquad (14)$$

$$2HSO_3^{-1} \overset{K_3}{\rightleftharpoons} H_2O + S_2O_5^{-2} \qquad (15)$$

K_H is Henry's constant and K_1, K_2 are acid dissociation constants. K_3 is the formation constant for $S_2O_5^{2-}$ at 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 (7.9 - 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 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 catalyzed reaction is highly decelerated by the addition of IPA like that of ethanol reported by Gupta *et al* [22] this indicates the operation of a radical mechanism involving oxysulphur free radicals, like SO_3^-, SO_4^- and SO_5^- . The inhibition is caused through the scavenging of SO_4^- by inhibitors such as ethanol and benzene, etc. As reported by Sharma *et al* [23-28] 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 be 4.9×10^3, which lies in the same range. This strongly supports the radical mechanism for the Co_2O_3 – catalyzed reaction in presence of IPA. Based on the observed results including the inhibition by IPA, the following radical mechanism is proposed which similar to that proposed by Manoj*et al* [29] sameena *et al* [30] in the ethanol inhibition of the CoO catalyzed reaction.

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

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

$$Co_2O_3.\ SO_3^{2-}.O_2 \xrightarrow{k_1} Co_2O_3 + SO3^{-} + O_2^{-} \qquad (18)$$

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

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

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

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

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

$$SO_4^{-} + x \xrightarrow{k_7} \text{Nonchain product} \qquad (24)$$

$$SO_4^{-} + IPA \xrightarrow{k_8} \text{Nonchain product} \qquad (25)$$

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. 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. (Eq. 26)

$$k_1[Co_2O_3(SO_3^{2-})(O_2)] = \{k_7[X]+k_8[IPA]\}[SO_4^-] \qquad (26)$$

Since the reaction is completely stopped in the presence of [IPA] at 1.56×10^{-3}mol L^{-1}. So the steps (18) & (22) appear to be unimportant. The contribution of propagation reaction (21) been significant in the Co_2O_3 catalyzed. Reaction where the autoxidation reaction should have occurred even in the presence of high iso propyl alcohol concentration. But this is not true and the reaction is completed seized in the presence of high concentration of iso propyl alcohol. This led us to ignore the step (21) and assume only the rate of reaction given by equation (27).

$$-d[S(IV)]/dt = R_{cat} = k_6 [SO_4^-] [SO_3^{2-}] \qquad (27)$$

By substituting the value of (SO_4^-) we get

$$R_{cat} = \frac{k_6 k_1 [Co_2O_3.\ SO_3^{2-}.O_2] [SO_3^{2-}]}{k_7[x] + k_8 [IPA]} \qquad (28)$$

From equilibrium 13 & 14

$$R_{cat} = \frac{k_6K_2\ K_1 [Co_2O_3] [S(IV)] [O_2]}{1 + k_1[s\ (IV)] \{k_7 [x] + k_8 [IPA]\}} \qquad (29)$$

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

$$R_{cat} = \frac{k^1 [Co_2O_3] [S\ (IV)]}{\{1 + k_1[s\ (IV)] \{k_7 [x] + k_8 [IPA]\}} \qquad (30)$$

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

$$R_{cat} = \frac{k^1 [Co_2O_3]\ [S(IV)]}{k_7 [x] + k_8 [IPA]} \qquad (31)$$

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 3.8×10^4 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 aniline act as a free radical scavenger in the Co_2O_3 catalysed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system [31-32].

6. CONCLUSIONS

The role of IPA 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.

$$-d[S(lV)]/dt = (k_1 + k_2[Co_2O_3])\ [S(lV)]/1 + B\ [IPA]$$

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 IPA. The effect of pH on SO_2 oxidation in the presence of Co_2O_3 and IPA has been studied and found rate of the SO_2 oxidation independent of the pH change during the reaction. The effect of temperature of the solution on SO_2 oxidation catalysed by Co_2O_3in the presence of IPA was discussed. Our results conclusively shows that *benzamide* studied here act as an inhibitor not a catalyst for SO_2 autoxidation.

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