Co$_2$O$_3$ Catalyzed Oxidation of SO$_2$ in Aqueous Solution
Differing Effect of Benzamide in Alkaline Medium

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Abstract: We report that benzamide is a good inhibitor for SO$_2$ oxidation in the pH range 7.8-9.4 in the presence of Co$_2$O$_3$. Based on the observed results the following rate law is given and a free radical mechanism has been proposed. -d[S(IV)]/dt = (k$_1$+k$_2$[Co$_2$O$_3$]) [S(IV)]/1+B [benzamide]. Experiments were carried out at 30 ≤ T °C ≤ 40, 7.8 ≤ pH ≤ 9.4, 1×10$^{-3}$ mol/dm$^3$ ≤ [S(IV)] ≤ 6×10$^{-3}$ mol/dm$^3$, 0.1 g/L ≤ [Co$_2$O$_3$] ≤ 0.4g/L, 1×10$^{-3}$mol/dm$^3$ ≤ [benzamide] ≤ 5×10$^{-3}$ mol/dm$^3$. Rate constants and the order of reaction were calculated and the reaction was found to be pseudo-first order in all cases. The effect of pH and temperature are also discussed. The value of apparent activation (E$_a$) energy was determined to be 8.7 kJ mol$^{-1}$. The activation of energy was calculated by Arrhenius equation. (k = A e$^{-Ea/RT}$).

Keywords: Kinetics, Autoxidation, SO$_2$, Co$_2$O$_3$, Catalysis, Inhibition, Benzamide

Introduction

The transformation of sulfur dioxide to acid sulphate 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$_2$O$_2$, which are produced in the atmosphere by photochemical reactions, and oxidation by O$_2$ in aqueous phase catalyzed by dissolved trace metal ions and by suspended particulate matter are major contributors to acid precipitation$^{1,2}$. The metal oxides are released to the atmosphere as a result of combustion processes are therefore important constituents of suspended particulate matter. The catalytic role of several metal oxides such$^{3-8}$ as CoO; Co$_2$O$_3$; Ni$_2$O$_3$; CuO; MnO$_2$ and Cu$_2$O; waste product of water treatment plants containing$^{9,10}$ CaO cobalt ions$^{11}$ and carbon nanotubes$^{12}$, transition metal catalyst$^{13}$ and cobalt based molecular sieves$^{14}$ has been reported. Conklin and Hoffman$^{15}$ proved that the liquid phase oxidation of SO$_2$ has been established as a major pathway in the biogeochemical sulfur cycle and in the production of acidity in the atmosphere.

The S(IV) autoxidation reaction is known to proceed via both radical and non-radical mechanisms$^{16-18}$. An interesting feature of many radical reactions is that, the reaction rate is
inhibited by organics such as acetic acid, oxalic acid\textsuperscript{19}, alcohols\textsuperscript{20}, carboxylic acid\textsuperscript{21}, formic acid, isopropyl alcohol, isoamyl alcohol, aniline, benzamide, sodium benzoate\textsuperscript{22-27}, ascorbic acid\textsuperscript{28}, organic compounds\textsuperscript{29}, VOC\textsuperscript{30} and diesel truck particles\textsuperscript{31}.

In Indian subcontinent the pH of the rain water lies in the range 6.5-8.5. This necessitates a study of the S(IV) autoxidation in the alkaline pH range. In most of the studies the role of organics has been reported in the metal ion catalyzed autoxidation of S(IV) in aqueous medium. Very few studies are available on the role of organics on the metal oxide catalyzed autoxidation of S(IV) in aqueous medium. This led us to investigate the kinetics of S(IV) autoxidation catalyzed by Co\textsubscript{2}O\textsubscript{3} in the pH range 7.8-9.4 and the effect of benzamide has been studied in alkaline media to delineate the nature of the mechanism.

**Experimental**

The experimental procedure was exactly the same as described earlier\textsuperscript{32} 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 °C. The reactions were initiated by adding the desired volume of standard Na\textsubscript{2}SO\textsubscript{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 was studied in buffered medium, in which the pH remained fixed throughout the entire course of reaction. For this purpose, 10 cm\textsuperscript{3} of buffer made from Na\textsubscript{2}HPO\textsubscript{4} (0.08 mol L\textsuperscript{-1}) and KH\textsubscript{2}PO\textsubscript{4} (0.02 mol L\textsuperscript{-1}) for alkaline medium were used (total volume 100 m\textsuperscript{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.

**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 S(IV). When the reaction was complete, Co\textsubscript{2}O\textsubscript{3} was filtered out and sulphate was estimated gravimetrically by precipitating sulphate ions as BaSO\textsubscript{4} using standard procedure\textsuperscript{33}.

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

\[
\text{S(IV)} + 0.5\text{O}_2 \rightarrow \text{S(VI)}
\]

**Results and Discussion**

**Preliminary investigation**

The kinetics of both uncatalysed and Co\textsubscript{2}O\textsubscript{3} catalyzed reaction were studied in alkaline medium in the pH range 7.8-9.4. 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 Figure 1.
Figure 1. The disappearance of [S(IV)] with time in air – saturated suspensions at [S(IV)] = 2×10^{-3} mol dm^{-3}, at 30 °C and pH = 7.88, (■) Co_{2}O_{3} = 20 mg, benzamide = 0 mL, (●) un catalysed and without benzamide (▲) Co_{2}O_{3} = 20 mg, benzamide = 5×10^{-3} mol dm^{-3}

Uncatalysed reaction
This study was done in the absence of catalyst.

Dependence of sulphite
The detailed dependence of the reaction rate on [S(IV)] was studied by varying it 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 Figure 1, log [S(IV)] vs. 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 Eq. 2.

\[ -d[S(IV)]/dt = k_{1} [S(IV)] \] (2)

Table 1. Values of k_{1} for un catalysed reaction at different [S(IV)] at pH= 7.34 and T = 30 °C

<table>
<thead>
<tr>
<th>[S(IV)] mol dm^{-3}</th>
<th>10^{4}k_{1} s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>10.5</td>
</tr>
<tr>
<td>0.002</td>
<td>10.6</td>
</tr>
<tr>
<td>0.004</td>
<td>10.1</td>
</tr>
<tr>
<td>0.006</td>
<td>10.5</td>
</tr>
</tbody>
</table>

[Benzamide] dependence
The major aim of this study was to examine the effect of organic inhibitors on the reaction rate, benzamide was chosen as the third inhibitor. On increasing the concentration of benzamide from 1×10^{-3} mol dm^{-3} to 5×10^{-3} mol dm^{-3}, the rate of reaction decreased. The pseudo- first order rate constant k_{inh} in the presence of benzamide is defined by rate law Eq. 3.

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

It was observed that when we increased the benzamide concentration then the rate constants k_{inh} decreased which is in agreement with the rate law Eq. 4

\[ k_{inh} = k_{1}/(1+B[Benzamide]) \] (4)

Where B is inhibition parameter for rate inhibition by benzamide.
The Eq. 4 on rearrangement becomes

\[ \frac{1}{k_{\text{inh}}} = \frac{1}{k_1} + B \frac{[\text{Benzamide}]}{k_1} \]  

(5)

In accordance with Eq. 5 the plot of \( \frac{1}{k_{\text{inh}}} \) vs. [Benzamide] was found to be linear with a non-zero intercept, Figure 2. The values of intercept \((1/k_1)\) and slope \((B/k_1)\) were found to be \(1.22 \times 10^2 \text{ s} \) and \(2.30 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s} \) at \(\text{pH} = 7.88\) and \(30 ^\circ \text{C}\). From these values the value of inhibition parameter \(B\) was found to be, \(1.89 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \).

**Figure 2.** Effect of benzamide at \([\text{S(IV)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}\) and at \(30 ^\circ \text{C}\) in phosphate buffered medium

**Co}_3_2O_3 Catalyzed reaction**

At first the kinetics of \(\text{Co}_3_2O_3\) catalyzed reaction in the absence of benzamide was studied.

**[S(IV)] Variation**

The concentration of \(\text{S(IV)}\) was varied from \(1 \times 10^{-3} \text{ mol dm}^{-3}\) to \(10 \times 10^{-3} \text{ mol dm}^{-3}\) at two different but fixed \([\text{Co}_3_2O_3]\) of 0.1 and 0.2 g L\(^{-1}\) was carried out at \(\text{pH} = 7.34\) and \(T=30 ^\circ \text{C}\). The kinetics was found to pseudo-first order in both cases.

**[Co}_3_2O_3] Variation**

The effect of \([\text{Co}_3_2O_3]\) on the rate was studied and the values of first order rate constants \(k_{\text{cat}}\) for \(\text{S(IV)}\)-autotioxidation was determined at different \([\text{Co}_3_2O_3]\) at \(\text{pH}=7.34\), \(T=30 ^\circ \text{C}\). The results are given in Table 2.

**Table 2.** The value of \(k_{\text{cat}}\) at different \([\text{Co}_3_2O_3]\) at \(\text{pH} = 7.80\) and \(T = 30 ^\circ \text{C}\)

<table>
<thead>
<tr>
<th>([\text{Co}_3_2O_3], \text{ g L}^{-1})</th>
<th>(10^3 k_{\text{cat}}, \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>8.8</td>
</tr>
<tr>
<td>0.2</td>
<td>13.7</td>
</tr>
<tr>
<td>0.3</td>
<td>16.9</td>
</tr>
<tr>
<td>0.4</td>
<td>21.8</td>
</tr>
</tbody>
</table>

It follows a rate law given in the Eq. 6.

\[-d [\text{S(IV)}]/dt = k_{\text{cat}} [\text{S(IV)}] = (k_1 + k_2[\text{Co}_3_2O_3]) [\text{S(IV)}]\]

(6)

\[k_{\text{cat}} = k_1 + k_2[\text{Co}_3_2O_3]\]

(7)

The values of intercept is equal to \(k_1\) and slope is equal to \(k_2\) were found to be \(5.1 \times 10^{-4} \text{ s}\) and \(4.01 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}\). 


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 3. The effect of \([\text{buffer}]\) was examined by varying the concentration of both \(\text{Na}_2\text{HPO}_4\) and \(\text{KH}_2\text{PO}_4\) in such a way that the ratio \(\text{[Na}_2\text{HPO}_4] / \text{[KH}_2\text{PO}_4]\) remained same, so that pH remained fixed. The values showed that the rate of the reaction to be insensitive to the buffer concentration.

Table 3. Variation of pH at \([\text{Co}_2\text{O}_3] = 0.2 \text{ g L}^{-1} , \text{[S(IV)]} = 2 \times 10^{-3} \text{ mol dm}^{-3}\) and \(T = 30 \degree \text{C}\)

<table>
<thead>
<tr>
<th>([\text{S(IV)] mol dm}^{-3} )</th>
<th>([\text{Co}_2\text{O}_3] \text{ g L}^{-1} )</th>
<th>([\text{Benzamide}] \text{ mol dm}^{-3} )</th>
<th>pH</th>
<th>Temp. (\degree \text{C} )</th>
<th>(10^3 \text{[kcat \text{[Co}_2\text{O}_3]}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.003 M</td>
<td>7.90</td>
<td>30 \degree \text{C}</td>
<td>5.07</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.003 M</td>
<td>8.15</td>
<td>“</td>
<td>5.22</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.003 M</td>
<td>8.55</td>
<td>“</td>
<td>5.24</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.003 M</td>
<td>9.45</td>
<td>“</td>
<td>5.09</td>
</tr>
</tbody>
</table>

Rate law in the presence of benzamide

A detailed study of dependence of rate on \([\text{S(IV)]}, [\text{Co}_2\text{O}_3]\) and pH on the reaction in the presence of benzamide revealed that the kinetics remain first order both in \([\text{S(IV)]}\) and \([\text{Co}_2\text{O}_3]\) and independent of pH in agreement with the following rate law.

By increasing the sodium benzoate concentration the rate decelerates i.e., inhibition occurs. The results are shown in Table 4 and the effect of \([\text{Co}_2\text{O}_3]\) in the presence of benzamide is shown in Figure 3. The dependence of the observed results for the reaction follows the following rate law Eq. 8.

\[
-d [\text{S(IV)]} / dt = (k_1 + k_2 [\text{Ag(I)]}) [\text{S(IV)]} / 1 + B [\text{Benzamide}],
\]

Where,

\[
k_{inh} = (k_1 + k_2 [\text{Ag(I)]}) / 1 + B [\text{Benzamide}] = k_{cat} / 1 + B [\text{Benzamide}]
\]

\[
1/ k_{inh} = 1/ k_{cat} + B [\text{Benzamide}] / k_{cat}.
\]

\[
1/ k_{inh} = 1/ k_{cat} + B [\text{Benzamide}] / k_{cat}.
\]

A plot between \([\text{Co}_2\text{O}_3] \text{ vs.} \) first order rate constant is linear Figure 3 with intercept 1.65×10^{-3} \text{ s}^{-1} and slope 6.21×10^{-4} \text{ g}^{-1} \text{ L} \text{ s}^{-1}.

Figure 3. Effect of \([\text{S(IV)]} \text{ at benzamide = 3×10}^{-3} \text{ g L}^{-1}, \text{pH=7.34 and at 30 \degree \text{C}, in phosphate buffered medium.}

A plot between 1/k_{inh} vs. [benzamide] is linear with intercept = 6.83×10^{2} \text{ s and slope = 1.05×10^{6}mol}^{-1} \text{ dm}^{-3} \text{ s from which the value of B = 1.5×10^{3}mol}^{-1} \text{ dm}^{-3}.
Table 4. The variation of [benzamide] at [S(IV)] = 2×10^{-3} \text{ mol dm}^{-3}, [Co_2O_3] = 0.1 \text{ g L}^{-1}, T = 30 ^\circ\text{C} and pH = 7.34

<table>
<thead>
<tr>
<th>[Benzamide]</th>
<th>k_{inh}</th>
<th>1/k_{inh}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.01 \times 10^{-4}</td>
<td>990</td>
</tr>
<tr>
<td>1\times 10^{-3}</td>
<td>5.7 \times 10^{-4}</td>
<td>1754</td>
</tr>
<tr>
<td>2\times 10^{-3}</td>
<td>4.06 \times 10^{-4}</td>
<td>2439</td>
</tr>
<tr>
<td>3\times 10^{-3}</td>
<td>2.79 \times 10^{-4}</td>
<td>3571</td>
</tr>
<tr>
<td>5\times 10^{-3}</td>
<td>1.63 \times 10^{-4}</td>
<td>6250</td>
</tr>
</tbody>
</table>

Effect of temperature

The values of k_{obs} were determined at three different temperatures in the range 30 to 40 °C the results given in Table 5. These values yielded an apparent empirical energy of activation 8.70 kJ mol^{-1}.

Table 5. Effect of temperature on k_{obs} in air saturated suspensions at [S(IV)] = 2×10^{-3} \text{ mol dm}^{-3}, [Co_2O_3] = 0.2 \text{ g L}^{-1}, [benzamide] = 3×10^{-3} \text{ mol dm}^{-3}, T = 30 ^\circ\text{C} and pH = 7.34

<table>
<thead>
<tr>
<th>T °C</th>
<th>10^4k_{obs} \text{ s}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>5.07</td>
</tr>
<tr>
<td>35</td>
<td>6.62</td>
</tr>
<tr>
<td>40</td>
<td>8.47</td>
</tr>
</tbody>
</table>

In aqueous solution SO_2 is present in four forms, SO_2H_2O, HSO_3^{-}, SO_3^{2-} and S_2O_5^{2-}, governed by the following equations.

\[
\text{SO}_2(g) + \text{H}_2\text{O} \xrightleftharpoons[K_{H}]{K_{1}} \text{SO}_2\text{H}_2\text{O(aq.)}
\]

\[
\text{SO}_2\text{H}_2\text{O(aq.)} \xrightleftharpoons[K_{1}]{K_{2}} \text{HSO}_3^{-1} + \text{H}^{+}
\]

\[
\text{HSO}_3^{-1} \xrightleftharpoons[K_{2}]{K_{3}} \text{H}^{+} + \text{SO}_3^{2-}
\]

\[
2\text{HSO}_3^{-1} \xrightarrow{K_{3}} \text{H}_2\text{O} + \text{S}_2\text{O}_5^{2-}
\]

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 \text{ mol L}^{-1} \text{ atm}^{-1}, K_{1}=1.4 \times 10^{-2}, K_{2}=6.24 \times 10^{-8} and K_{3}=7.6 \times 10^{-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 several transition metal oxide catalyzed heterogeneous aqueous phase auto oxidation reactions of S(IV), the formation of surficial complexes by adsorption of S(IV) and O_2 on the particle surface and oxidation of S(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), Halperin and Taube proposed that the sulphite 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 catalyzed reaction is highly decelerated by the addition of benzamide like that of ethanol reported by Gupta et al., this indicates the operation of a radical mechanism involving oxysulphur free radicals, like SO_3^{2-}, SO_4^{2-} and SO_5^{2-}. The inhibition is caused through the scavenging of SO_4^{2-} by inhibitors such as ethanol and benzene, etc.
As reported by Sharma\textsuperscript{36} and Mudgal\textsuperscript{37} 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 $2.46 \times 10^3$, which lies in the same range. This strongly supports the radical mechanism for the Co$_2$O$_3$ catalyzed reaction in presence of benzamide. Based on the observed results including the inhibition by benzamide, the following radical mechanism is proposed which similar to that proposed by Manoj \textit{et al.},\textsuperscript{38} Sharma \textit{et al.},\textsuperscript{39-41} Sameena \textit{et al.},\textsuperscript{42} in the ethanol inhibition of the CoO catalyzed reaction.

\begin{align*}
\text{Co}_2\text{O}_3 + \text{SO}_3^{2-} & \overset{K_1}{\rightleftharpoons} \text{Co}_2\text{O}_3\cdot \text{SO}_3^{2-} \quad (16) \\
\text{Co}_2\text{O}_3\cdot \text{SO}_3^{2-} + \text{O}_2 & \overset{K_2}{\rightarrow} \text{Co}_2\text{O}_3\cdot \text{SO}_3^{2-} \cdot \text{O}_2 \quad (17) \\
\text{Co}_2\text{O}_3\cdot \text{SO}_3^{2-} \cdot \text{O}_2 & \overset{k_1}{\rightarrow} \text{Co}_2\text{O}_3\cdot \text{SO}_3^{2-} + \text{O}_2 \quad (18) \\
\text{SO}_3^{2-} + \text{O}_2 & \overset{k_2}{\rightarrow} \text{SO}_5^- \quad (19) \\
\text{SO}_3^- + \text{SO}_3^{2-} & \overset{k_3}{\rightarrow} \text{SO}_5^{2-} + \text{SO}_3^- \quad (20) \\
\text{SO}_5^- + \text{SO}_3^{2-} & \overset{k_4}{\rightarrow} \text{SO}_5^{2-} + \text{SO}_3^- \quad (21) \\
\text{SO}_5^{2-} + \text{SO}_3^{2-} & \overset{k_5}{\rightarrow} 2\text{SO}_4^{2-} \quad (22) \\
\text{SO}_4^{2-} + \text{SO}_3^{2-} & \overset{k_6}{\rightarrow} \text{SO}_4^{2-} + \text{SO}_3^- \quad (23) \\
\text{SO}_4^- + x & \overset{k_7}{\rightarrow} \text{Nonchain product} \quad (24) \\
\text{SO}_4^- + \text{benzamide} & \overset{k_8}{\rightarrow} \text{Nonchain product} \quad (25)
\end{align*}

In the mechanism, no role is assigned to O$_2^-$, which is also known to react with S(IV) slowly. It may disproportionate to form H$_2$O$_2$ and O$_2$ or may be scavenged by impurities. By assuming long chain hypothesis and steady state approximation $d[\text{SO}_3^-]/dt$, $d[\text{SO}_4^-]/dt$ and $d[\text{SO}_5^-]/dt$ to zero it can be shown that the rate of initiation is equal to the rate of termination. (Eq. 26)

\begin{equation}
k_1[\text{Co}_2\text{O}_3(\text{SO}_3^{2-})(\text{O}_2)] = \{k_7[X]+k_8[\text{benzamide}]\}[\text{SO}_4^-] \quad (26)
\end{equation}

Since the reaction is completely stopped in the presence of [benzamide] at $1.2 \times 10^{-2}$ mol L$^{-1}$. So the steps (Eq. 18) and (Eq. 22) appear to be unimportant.

The contribution of propagation reaction (Eq. 21) been significant in the Co$_2$O$_3$ catalyzed. Reaction where the autoxidation reaction should have occurred even in the presence of high benzamide concentration. But this is not true and the reaction is completed seized in the presence of high concentration of benzamide. This led us to ignore the step (Eq. 21) and assume only the rate of reaction given by equation (Eq. 27).

\begin{equation}
-d[\text{S(IV)}]/dt = R_{\text{cat}} = k_6[\text{SO}_4^-][\text{SO}_2^{2-}] \quad (27)
\end{equation}

By substituting the value of (SO$_4^-$) we get

\begin{equation}
R_{\text{cat}} = \frac{k_6k_1[\text{Co}_2\text{O}_3\cdot \text{SO}_3^{2-}\cdot \text{O}_2][\text{SO}_3^{2-}]}{k_7[X]+k_8[\text{benzamide}]} \quad (28)
\end{equation}

From equilibrium Eq. 13 and Eq. 14
At fixed $\text{O}_2$, replacing $k_6, k_1, k_2[\text{O}_2]$ by $k^1$ we get

$$R_{\text{cat}} = \frac{k_1^1 [\text{Co}_2\text{O}_3][\text{S(IV)}] [\text{O}_2]}{[1 + k_1^1 [\text{S(IV)}][k_{j_1}[x] + k_8 \text{[benzamide]]}]$$

(29)

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

$$R_{\text{cat}} = \frac{k_1^1 [\text{Co}_2\text{O}_3][\text{S(IV)}]}{k_{j_1}[x] + k_8 \text{[benzamide]}}$$

(30)

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 $1.5 \times 10^3 \text{mol}^{-1} \text{dm}^3$ which is in the range of $10^3$ to $10^4$. So on the base of calculated value of $B$, we concluded that benzamide act as a free radical scavenger in the $\text{Co}_2\text{O}_3$ catalyzed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system.

**Conclusion**

The role of benzamide act as an inhibitor in $\text{Co}_2\text{O}_3$ catalysed autoxidation of $\text{SO}_2$ in alkaline medium has been found and based on the observed results rate law a free radical mechanism has been proposed.

$$-d[S(\text{IV})]/dt = (k_1 + k_2[\text{Co}_2\text{O}_3]) [S(\text{IV})]/1 + B \text{[Benzamide]}$$

Based on the experimental results, rate constants and orders of the reactions were determined. The reaction order in $\text{SO}_2$ was pseudo- first order for both reactions in the presence and absence of benzamide. The effect of pH on $\text{SO}_2$ oxidation in the presence of $\text{Co}_2\text{O}_3$ and benzamide has been studied and found rate of the $\text{SO}_2$ oxidation independent of the pH change during the reaction. The effect of temperature of the solution on $\text{SO}_2$ oxidation catalysed by $\text{Co}_2\text{O}_3$ in the presence of benzamide was discussed. By the plotting a graph between log k v/s 1/T yield us an apparent empirical energy of activation 8.7 kJ mol$^{-1}$ for the reaction. Our results conclusively shows that benzamide studied here act as an inhibitor not a catalyst for $\text{SO}_2$ autoxidation. The values of inhibition factor (B) for both uncatalysed and Ag(I) catalysed autoxidation of $\text{SO}_2$ in the presence of benzamide are $1.89 \times 10^4$ and $1.50 \times 10^3$ respectively which coincide with earlier workers who found inhibition factors in the range of $10^3$-$10^4$. Benzamide is able to inhibit the oxidation of $\text{SO}_2$ so by using it in the atmosphere rain water acidity can be controlled.

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