Effect of Acetic Acid on Co$_2$O$_3$ Catalyzed Autoxidation of Aqueous Sulphur Dioxide in Alkaline Medium

Sharma H, Sharma AK, Parasher P, Prasad DSN*

Department of Chemistry, Govt. P. G. College, Jhalawar- 326001, Rajasthan India

*Corresponding author: Prasad DSN

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Abstract

The kinetics of the acetic acid inhibited Co$_2$O$_3$ catalysed autoxidation of S (IV) in alkaline medium has been studied and based on the observed results following rate has been proposed. 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 by Arrhenius equation. On the basis of inhibition parameters the reaction follows free radical mechanism.

Keywords: Kinetics; Autoxidation; SO$_2$; Co$_2$O$_3$; Catalysis; Inhibition; acetic acid.

INTRODUCTION

The atmospheric reactions of SO$_2$ and NO$_x$ etc. are major acid rain precursors and are responsible for acidification of various forms of atmospheric water [1]. Studies our country the level of SO$_2$ in atmospheric environment is increasing gradually and therefore the danger of acid rain cannot be simply under estimated [2]. 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 in to acids such as HNO$_2$, HNO$_3$, H$_2$SO$_3$ and H$_2$SO$_4$.

The catalytic role of several metal oxides such as CoO[3]; Co$_2$O$_3$[4]; Ni$_2$O$_3$[5]; CuO[6]; MnO$_2$[7]; and Cu$_2$O[8] in acidic medium has been reported. The S (IV) autoxidation reaction is known to proceed via both radical and non-radical mechanisms [9].

An interesting feature of many radical reactions is that, the reaction rate is inhibited by organics such as acetic acid, oxalic acid [10], alcohols [11], carboxylic acid [12], and ammonia [13], formic acid, isopropyl alcohol, isoamyl alcohol, aniline, benzamide, sodium benzoate [14-20]. In Indian sub-continent, the pH of the rain water lies in the range 6.5-8.5 this necessitates the study of autoxidation of S (IV) in alkaline medium. This led us to investigate the kinetics of S (IV) autoxidation catalyzed by Co$_2$O$_3$ in the pH range 7.3-9.4 and so the effect of acetic acid on this reaction has been studied to know the nature of mechanism.

EXPERIMENTAL

The experimental procedure was exactly same as described earlier by Prasad et al. [21]. All calculations were performed in MS Excel.

Product Analysis

When the reaction was complete, Co$_2$O$_3$ was filtered out and sulphate was estimated gravimetrically by precipitating sulphate ions as BaSO$_4$ using standard procedure [22].
The product analysis showed the recovery of sulfate to be 98 ± 2% in all cases in agreement with Eq. (1)

\[
S(IV) + 0.5 O_2 \rightarrow S(VI)
\]  \hspace{1cm} (1)

**RESULTS**

**Preliminary Investigation**

The kinetics of both uncatalyzed and Co$_2$O$_3$ catalyzed reaction were studied in alkaline medium in the pH range 7.8-9.4. In both cases, first order was found in [S(IV)] and the treatment of kinetics data first order rate constant $k_1$. It was determined 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)] = 2×10^{-3} \text{ mol L}^{-1}, \text{at } 30^\circ \text{C and pH = 7.80}**

**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} \text{ mol dm}^{-3} to 6×10^{-3} \text{ mol dm}^{-3} at pH= 7.80, $t = 30^\circ \text{C in phosphate buffer medium.}$ The kinetics was found to be pseudo first order in [S(IV)] as shown in fig.1, log [S(IV)] 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)] and are in agreement with the rate law (2).

\[
-k_1 \frac{d[S(IV)]}{dt} = k_1 [S(IV)]
\]  \hspace{1cm} (2)

**Table-1: The values of $k_1$ for uncatalysed reaction at different [S(IV)] at pH= 7.80 and $t = 30^\circ \text{C}**

<table>
<thead>
<tr>
<th>[S(IV)] \text{mol L}^{-1}</th>
<th>10^3 k_1 \text{ s}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>1.06</td>
</tr>
<tr>
<td>0.002</td>
<td>1.07</td>
</tr>
<tr>
<td>0.004</td>
<td>1.01</td>
</tr>
<tr>
<td>0.006</td>
<td>1.05</td>
</tr>
</tbody>
</table>

**[Acetic acid] dependence**

The major aim of this study was to examine the effect of organic inhibitors on the reaction rate, acetic acid was chosen as the one organic compound. On increasing the concentration of acetic acid from 5×10^{-6} to 5×10^{-3} \text{ mol L}^{-1}, the rate of reaction decreased.

However, the nature of the [S(IV)] – dependence in presence of acetic acid did not change and remained first order. The first order rate constant $k_{inh}$, were defined by rate law (3).
\[
-d\left[\text{S(IV)}\right]/dt = k_{\text{inh}}\left[\text{S(IV)}\right]
\]

(3)

\[
\frac{1}{k_{\text{inh}}} = \frac{1}{k_1} + B \times \text{[acetic acid]} / k_1
\]

(4)

Where B is inhibition parameter for rate inhibition by acetic acid.

The equation (4) on rearrangement becomes

\[
\frac{1}{k_{\text{inh}}} = \frac{1}{k_1} + B \times \text{[acetic acid]} / k_1
\]

(5)

In accordance with eq. (5) the plot of \(1/k_{\text{inh}}\) versus [acetic acid] 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 \(2.16 \times 10^2\ s\) and \(6.89 \times 10^9\ mol^{-1} L\ s\) at \(pH=7.80\), and 30°C. From these values the value of inhibition parameter B was found to be \(3.17 \times 10^7\ mol^{-1}\ L\).

**Co\textsubscript{2}O\textsubscript{3}** - Catalyzed Reaction

At first the kinetics of Co\textsubscript{2}O\textsubscript{3}-catalyzed reaction in the absence of inhibitor was studied.

**[S (IV)] Variation**

[S(IV)] was varied from \(1 \times 10^{-3}\) to \(10 \times 10^{-3}\) mol L\(^{-1}\) at two different but fixed [Co\textsubscript{2}O\textsubscript{3}] of 0.1 and 0.2 g L\(^{-1}\) was carried out at \(pH=7.80\) and \(t=30^\circ C\). The results are given in Table 2. The kinetics was found to be first order in [S(IV)] as shown in Fig 1. The log [S (IV)] versus time plots was linear.

**[Co\textsubscript{2}O\textsubscript{3}] Variation**

The effect of [Co\textsubscript{2}O\textsubscript{3}] on the rate was studied and the values of first order rate constants \(k_{\text{cat}}\) for S (IV) - autoxidation was determined at different [Co\textsubscript{2}O\textsubscript{3}]. At \(pH=7.80, t=30^\circ C\). The results of \(k_{\text{cat}}\) are given in Table 2.
Table 2: The value of \( k_{\text{cat}} \) at different \([\text{Co}_2\text{O}_3]\) at \( \text{pH} = 7.80 \) and \( t = 30^\circ\text{C} \)

<table>
<thead>
<tr>
<th>([\text{Co}_2\text{O}_3](\text{g L}^{-1}))</th>
<th>(10^6 k_{\text{cat}} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.04</td>
</tr>
<tr>
<td>0.2</td>
<td>3.52</td>
</tr>
<tr>
<td>0.3</td>
<td>4.24</td>
</tr>
<tr>
<td>0.4</td>
<td>4.79</td>
</tr>
<tr>
<td>0.5</td>
<td>5.97</td>
</tr>
</tbody>
</table>

The nature of dependence of \( k_{\text{cat}} \) on \([\text{Co}_2\text{O}_3]\) indicates the operation of a two term rate law.

\[
-d [\text{S(IV)}]/dt = k_{\text{cat}} [\text{S(IV)}] = (k_1 + k_2[\text{Co}_2\text{O}_3]) [\text{S(IV)}]
\]  

\[k_{\text{cat}} = k_1 + k_2 [\text{Co}_2\text{O}_3]\]  

The values of intercept is equal to \( k_1 \) and slope is equal to \( k_2 \) were found to be 7.1 s and 4.1 mol\(^{-1}\) L s\(^{-1}\), respectively at \( \text{pH} = 7.80 \) and 30°C.

Variation of pH

Variation in pH in the range 7.80 to 9.4 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\(_2\)HPO\(_4\) & KH\(_2\)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 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 \([\text{Co}_2\text{O}_3] = 0.2 \text{ g L}^{-1}, [\text{S(IV)}] = 2\times10^{-3} \text{ mol L}^{-1} \) and \( t = 30^\circ\text{C} \)

<table>
<thead>
<tr>
<th>[S(IV)]molL(^{-1})</th>
<th>[Co(_2\text{O}_3)] g L(^{-1})</th>
<th>[acetic acid]molL(^{-1})</th>
<th>pH</th>
<th>temp.</th>
<th>(10^6 k_{\text{cat}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.0002 M</td>
<td>7.80</td>
<td>30°C</td>
<td>2.82</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.0002 M</td>
<td>8.50</td>
<td>30°C</td>
<td>2.92</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.0002 M</td>
<td>8.90</td>
<td>30°C</td>
<td>2.86</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2</td>
<td>0.0002 M</td>
<td>9.40</td>
<td>30°C</td>
<td>2.92</td>
</tr>
</tbody>
</table>

Rate Law in the Presence of acetic acid

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

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

\[k_{\text{inh}} = (k_1 + k_2[\text{Co}_2\text{O}_3]) / 1 + B [\text{acetic acid}] = k_{\text{cat}} / 1 + B [\text{acetic acid}] \]  

\[1/ k_{\text{inh}} = 1 + B [\text{acetic acid}] / k_{\text{cat}} \]  

\[1/ k_{\text{inh}} = 1/ k_{\text{cat}} + B [\text{acetic acid}] / k_{\text{cat}} \]

A plot between [Co\(_2\text{O}_3\)] v/s first order rates constant is linear (fig. 3) with intercept 1.93s\(^{-1}\) and slope 6.78 g\(^{-1}\) L s\(^{-1}\).
Fig-3: Effect of [Co$_2$O$_3$] at acetic acid = 3×10$^{-4}$ mol L$^{-1}$, pH=7.80 and at t = 30°C, in phosphate buffered medium.

Table-4: The variation of [acetic acid] at[S(IV)] = 2 × 10$^{-3}$ mol L$^{-1}$, [Co$_2$O$_3$] = 0.1 g L$^{-1}$, t = 30°C, and pH = 7.80

<table>
<thead>
<tr>
<th>[Acetic acid]</th>
<th>10$^{5}$k$_{inh}$ s$^{-1}$</th>
<th>1/k$_{inh}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10$^{-7}$</td>
<td>5.93</td>
<td>2057.61</td>
</tr>
<tr>
<td>2x10$^{-7}$</td>
<td>4.27</td>
<td>2702.7</td>
</tr>
<tr>
<td>4x10$^{-7}$</td>
<td>3.79</td>
<td>3215.43</td>
</tr>
<tr>
<td>6x10$^{-7}$</td>
<td>3.21</td>
<td>3496.5</td>
</tr>
<tr>
<td>2x10$^{-6}$</td>
<td>2.8</td>
<td>4608.29</td>
</tr>
<tr>
<td>4x10$^{-6}$</td>
<td>2.05</td>
<td>5347.59</td>
</tr>
<tr>
<td>8x10$^{-6}$</td>
<td>1.46</td>
<td>7352.94</td>
</tr>
<tr>
<td>1x10$^{-5}$</td>
<td>1.03</td>
<td>17543.85</td>
</tr>
</tbody>
</table>

A plot between 1/K$_{inh}$/s [acetic acid] is linear, with intercept = 2.08× 10$^{3}$ s and slope = 1.17× 10$^{8}$ mol$^{-1}$ L s from which the value of B = 5.64× 10$^{4}$ 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 4. These values yielded an apparent empirical energy of activation 37.65 kJ mol$^{-1}$.

Table-4: Effect of temperature on k$_{obs}$ air saturated suspensions at [S(IV)] = 2 × 10$^{-3}$ mol L$^{-1}$, [Co$_2$O$_3$] = 0.2 g L$^{-1}$, [acetic acid] =2×10$^{-4}$ mol L$^{-1}$, t = 30°C, and pH = 7.80

<table>
<thead>
<tr>
<th>t °C</th>
<th>10$^{5}$k$_{obs}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.31</td>
</tr>
<tr>
<td>35</td>
<td>5.19</td>
</tr>
<tr>
<td>40</td>
<td>6.98</td>
</tr>
</tbody>
</table>

**DISCUSSION**

In aqueous solution SO$_2$ is present in four forms, SO$_2$.H$_2$O, HSO$_3^-$, SO$_3^{2-}$ and S$_2$O$_5^{2-}$, governed by the following equations.
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 = 1.4×10^{-2}, K_2 = 6.24×10^{-8}, and K_3 = 7.6×10^{-2}. In this experimental study in pH range (7.8 - 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 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 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 catalysed reaction is highly decelerated by the addition of acetic acid like that of reported by Husain et al [23-26] this indicates the operation of a radical mechanism involving oxysulphur free radicals, like SO_3^{-}, SO_4^{2-} and SO_5^{2-}. The inhibition is caused through the scavenging of SO_3^{-} by inhibitors such as ethanol and benzene, etc.

As reported by Sameena et al. [27] a radical mechanism operates in those reactions in which the inhibition parameter lays the range 10^3-10^5. In this study the value of inhibitor parameter is found to be 5.82×10^5, which lies in the same range. This strongly supports the radical mechanism. For the Co_2O_3 – catalyzed reaction in presence of acetic acid. Based on the observed results including the inhibition by acetic acid, the following radical mechanism is proposed which similar to that proposed by Prasad et al [29] in the oxalic acid inhibition of the Co_2O_3 catalysed reaction.

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^{2-}]/dt and d[SO_5^{2-}]/dt to zero it can be shown that the rate of initiation is equal to the rate of termination.
\[
\text{k}_1 [\text{Co}_2\text{O}_3 (\text{SO}_3^2-) (\text{O}_2)] = \{\text{k}_7 [\text{X}] + \text{k}_8 [\text{acetic acid}]\} [\text{SO}_4^2-] \quad (27)
\]

Since the reaction is completely stopped in the presence of [acetic acid] at \(1 \times 10^{-3}\) mol L\(^{-1}\), so the steps (15) & (19) appear to be unimportant. The contribution of propagation reaction (18) been significant in the \(\text{Co}_2\text{O}_3\) catalyzed. Reaction where the autoxidation reaction should have occurred even in the presence of high acetic acid concentration. But this is not true and the reaction is completely seized in the presence of high concentration of acetic acid. This led us to ignore the step (18) and assume only the rate of reaction given by equation (28).

\[
\text{R}_{\text{est}} = \frac{\text{k}_1 [\text{Co}_2\text{O}_3] [\text{S} (\text{IV})]}{1 + \text{k}_1 [\text{S} (\text{IV})] + \text{k}_8 [\text{acetic acid}]} \quad (28)
\]

Sharma et al. [28-30] proposed a similar mechanism for the \(\text{Ag} (\text{I})\) catalysed autoxidation of sulfur dioxide inhibited by organics, which lead to the same rate law. By comparing derived rate law with the experimental rate we observe the similarity in these two. The calculated value of inhibition constant \(B\) is \(3.17 \times 10^5\) mol \(^{-1}\) L which is in the range of \(10^3\) to \(10^5\). So on the base of calculated value of \(B\) we concluded that acetic acid act as a free radical scavenger in the \(\text{Co}_2\text{O}_3\) catalysed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system.

**CONCLUSIONS**

The role of acetic 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.

\[
\frac{d[\text{S} (\text{IV})]}{dt} = (\text{k}_1 + \text{k}_2 [\text{Co}_2\text{O}_3]) [\text{S} (\text{IV})]/ 1 + B [\text{acetic acid}]
\]

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**REFERENCES**


