The Influence of Succinic Acid on the Kinetics of the Atmospheric Oxidation of Dissolved SO$_2$ Catalysed by Co$_2$O$_3$

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ABSTRACT: The kinetics of the succinic 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; succinic acid

I. INTRODUCTION

The aqueous-phase atmospheric oxidation of sulphur dioxide by oxygen contributes to acidification of atmospheric waters. It, therefore, has been the subject of numerous studies, and details can be found in reviews and books [1–2]. The oxidation of dissolved sulphur dioxide, hereafter referred to as sulphur(IV), proceeds through a radical mechanism involving sulfoxyl radicals [3-5]. The catalytic role of several metal oxides such as CoO [6]; Ni$_2$O$_3$ [7]; CuO [8]; MnO$_2$ [9]; and Cu$_2$O [10] in acidic medium has been reported. The S(IV) autoxidation reaction is known to proceed via both radical and non-radical mechanisms [11].

VOCs play a crucial role in tropospheric chemistry [12] through their reactions with hydroxyl, nitrate, and sulphate radicals. All kinds of VOCs such as aliphatic, aromatic, cyclic, polycyclic, heterocyclic, acyclic, saturated, unsaturated, oxygenated, halogenated, alcohols, terpenes, phenols, carbonyl compounds, carboxylic acids, esters, chloro-derivatives, etc. are found in the air, soil, and water environments [13-15].

An interesting feature of many radical reactions is that, the reaction rate is inhibited by organics such as acetic acid, oxalic acid [16], alcohols [17], carboxylic acid [18], and ammonia [19], formic acid, isopropyl alcohol, isoamyl alcohol, aniline, benzamide, sodium benzoate [20-25]. 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 succinic acid on this reaction has been studied to know the nature of mechanism.

II. EXPERIMENTAL

The experimental procedure was exactly same as described earlier by Prasad et al., [26]. All calculations were performed in MS Excel.

III. 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 [27].

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

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

IV. RESULTS

A. 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.
The detailed dependence of the reaction rate on $[S(IV)]$ was studied by varying $[S(IV)]$ in the range $1 \times 10^{-3}$ to $6 \times 10^{-3}$ mol dm$^{-3}$ at pH = 7.80, 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 $[S(IV)]$ and are in agreement with the rate law (2).

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

(2)

Table 1: The values of $k_1$ for uncatalysed reaction at different $[S(IV)]$ at pH = 7.80 and t = 30°C.

<table>
<thead>
<tr>
<th>$[S(IV)]$ mol L$^{-1}$</th>
<th>$10^3 k_1$ 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>

D. [Succinic acid] dependence

The major aim of this study was to examine the effect of organic inhibitors on the reaction rate, succinic acid was chosen as the one organic compound. On increasing the concentration of succinic acid from $1 \times 10^{-3}$ to $1 \times 10^{-5}$ mol L$^{-1}$, the rate of reaction decreased. However, the nature of the $[S(IV)]$ – dependence in presence of succinic acid did not change and remained first order. The first order rate constant $k_{inh}$ were defined by rate law (3)

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

(3)

The values of $k_{inh}$ decreased with increase in succinic acid in agreement with the rate law.

$$K_{inh} = k_1/(1 + B [succinic acid])$$

(4)

where $B$ is inhibition parameter for rate inhibition by succinic acid.

The equation (4) on rearrangement becomes

$$1/K_{inh} = 1/k_1 + B [succinic acid] / k_1$$

(5)

In accordance with Eq. (5) the plot of $1/k_{inh}$ versus $[succinic acid]$ was found to be linear with a non-zero intercept, Fig. 2.

![Fig. 1. The disappearance of $[S(IV)]$ with time in air-saturated suspensions at $[S(IV)] = 2 \times 10^{-3}$ mol L$^{-1}$, at 30°C and pH = 7.80.](image)

![Fig. 2. Effect of succinic acid at $[S(IV)] = 2 \times 10^{-3}$ mol L$^{-1}$ and at 30°C, in phosphate buffered medium.](image)

The values of intercepts($1/k_1$) and slope ($B/k_1$) were found to be $1.16 \times 10^{-1}$ and $4.68 \times 10^{-1}$ Ls at pH = 7.80, and 30°C. From these values the value of inhibition parameter $B$ was found to be $4.02 \times 10^{-1}$.

E. $Co_3O_4$-Catalyzed Reaction

At first the kinetics of $Co_3O_4$ catalyzed reaction in the absence of inhibitor was studied.

F. $[S(IV)]$ Variation

$[S(IV)]$ was varied from $1 \times 10^{-3}$ to $10 \times 10^{-3}$ mol L$^{-1}$, at two different but fixed $[Co_3O_4]$ of 0.1 and 0.2 g L$^{-1}$ was carried out at pH = 7.80 and t = 30°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 were linear.

G. $[Co_3O_4]$ Variation

The effect of $[Co_3O_4]$ on the rate was studied and the values of first order rate constants $k_{cat}$, for $S(IV)$ autoxidation was determined at different $[Co_3O_4]$ at pH = 7.80, t = 30°C. The results of $k_{cat}$ are given in Table 2.

Table 2: The value of $k_{cat}$ at different $[Co_3O_4]$ at pH = 7.80 and t = 30°C.

<table>
<thead>
<tr>
<th>$Co_3O_4$ (g L$^{-1}$)</th>
<th>$10^3 k_{cat}$ 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 $k_{cat}$ on $[Co_3O_4]$ indicates the operation of a two term rate law.

$$-d[S(IV)]/dt = k_{cat} [S(IV)] = k_1 + k_2 [Co_3O_4] [S(IV)]$$

(6)

$$K_{cat} = k_1 / k_2 [Co_3O_4]$$

(7)

The values of intercept is equal to $k_1$ and slope is equal to $k_2$ were found to be $7.1$ s and $4.1 \times 10^{-1}$ mol$^{-1}$ L s, respectively at Ph = 7.80 and 30°C.
H. 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 Na₂HPO₄ & KH₂PO₄ in such a way that the ratio [Na₂HPO₄] / [KH₂PO₄] 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 [Co₂O₃] = 0.2 g L⁻¹, [S(IV)] = 2 × 10⁻³ mol L⁻¹ and t = 30°C.

<table>
<thead>
<tr>
<th>[S(IV)]mol L⁻¹</th>
<th>[Co₂O₃] g L⁻¹</th>
<th>[Succinic acid] mol L⁻¹</th>
<th>pH</th>
<th>Temperature</th>
<th>10⁴kcat[k₉ + k₃[Co₂O₃]]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.002</td>
<td>0.2</td>
<td>0.0002 M</td>
<td>7.80</td>
<td>30°C</td>
<td>1.82</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>1.92</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>1.86</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>1.92</td>
</tr>
</tbody>
</table>

I. Rate Law in the Presence of succinic acid
A detailed study of dependence of rate on [S(IV)], [Co₂O₃], and pH in the presence of succinic acid revealed that the kinetics remain first order both in [S(IV)] and [Co₂O₃] and independent of pH obeys the following rate law.

\[-d[S(IV)]/dt = (k₁ + k₂ [Co₂O₃] [S(IV)]/1 + B [succinic acid] k_{inh} = (k₁ + k₂ [Co₂O₃]/1 + B) [succinic acid] = k_{cat}/1 + B [succinic acid] \]

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

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

A plot between [Co₂O₃] v/s first order rate constant is linear (fig. 3) with intercept 2.53s⁻¹ and slope 5.18 g⁻¹ L s⁻¹.

I. Effect of temperature
The values of kobs 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 60.99 kJ mol⁻¹.

Table 4: Effect of temperature on kobs air saturated suspensions at [S(IV)] = 2 × 10⁻³ mol L⁻¹, [Co₂O₃] = 0.2 g L⁻¹, [succinic acid] = 2 × 10⁻³ mol L⁻¹, t = 30°C, and pH = 7.80.

<table>
<thead>
<tr>
<th>t °C</th>
<th>10⁴kobs s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.48</td>
</tr>
<tr>
<td>35</td>
<td>5.34</td>
</tr>
<tr>
<td>40</td>
<td>7.36</td>
</tr>
</tbody>
</table>

V. DISCUSSION
In aqueous solution SO₂ is present in four forms, SO₂, H₂O, HSO₃², SO₃² and S₂O₅²⁻, governed by the following equations.

\[SO₂ + H₂O \rightleftharpoons K_{Hi} SOH₂O (aq.) \quad (13)\]

\[SO₂ + H₂O (aq.) \rightleftharpoons K_{Hi} HSO₃⁻ + H⁺ \quad (14)\]

\[HSO₃⁻ \rightleftharpoons K_{Hi} SO₃⁻ + H⁺ \quad (15)\]

\[2HSO₃⁻ \rightleftharpoons K_{Hi} S₂O₅²⁻ + H₂O \quad (16)\]

Kᵢ₃ is Henry’s constant and Kᵢ₁, Kᵢ₂ are acid dissociation constants.

Kᵢ₃ is the formation constant for S₂O₅²⁻ at 25°C the values are Kᵢ₃ = 1.23 mol L⁻¹ atm⁻¹, Kᵢ₁ = 1.4×10⁻⁸, Kᵢ₂ = 6.24 × 10⁻⁶, and Kᵢ₃ = 7.6 × 10⁻². In this experimental study in pH range (7.8 - 9.4), the formation of surficial complexes by adsorption of S(IV) and O₂ 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 O₂ on the particle surface of Co₂O₃ through the fast step.
The contribution of propagation reaction (18) been significant steps (15) & (19) appear to be unimportant. The reaction is completed seized in the presence of high organics, 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 $3.17 \times 10^{5}$ 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 succinic acid act as a free radical scavenger in the Co$_3$O$_4$ catalysed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system [34-36].

VI. CONCLUSIONS

The role of succinic act as an inhibitor in Co$_3$O$_4$ 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.

$$\frac{-d[S(IV)]}{dt} = \frac{(k_1 + k_2[CoO_3]) [S(IV)]}{1 + B [Succinic acid]}$$

VII. 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: This work has no conflict of interest.

REFERENCES


