The Influence of Succinic Acid on the Kinetics of the Atmospheric Oxidation of Dissolved SO_2 Catalysed by Co_2O_3

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ABSTRACT: The kinetics of the succinic acid inhibited Co_2O_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.

$$R_{cat} = \frac{k_1 \, [Co_2O_3] \, [S(IV)]}{\{k_9[x] + k_{10}[\text{Succinic acid}]\}}$$

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 sulfoxy radicals [3-5]. The catalytic role of several metal oxides such as CoO [6]; Ni_2O_3 [7]; CuO [8]; MnO_2 [9]; and Cu_2O [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_2O_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_2O_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 $98 \pm 2\%$ in all cases in agreement with Eq. (1)

$$S(IV) + 0.5O_2 \rightarrow S(VI) \tag{1}$$
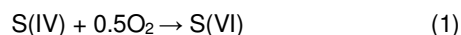
IV. RESULTS

A. Preliminary Investigation
The kinetics of both uncatalyzed and Co_2O_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
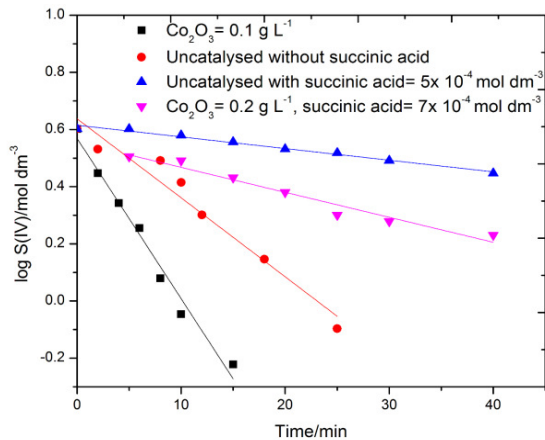
Fig. 1. The disappearance of [S(IV)] with time in air - saturated suspensions at [S(IV)] = 2 × 10⁻³ mol L⁻¹, at 30°C and pH = 7.80.

B. Uncatalysed Reaction
This study was done in the absence of catalyst.

C. 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 = 7.80, 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).

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

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

[S(IV)]mol L⁻¹	$10^5 k_1$ s⁻¹
0.001	1.06
0.002	1.07
0.004	1.01
0.006	1.05

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 1×10^{-7} to 1×10^{-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)

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

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

$$K_{inh} = k_1/(1 + B [\text{succinic acid}]) \qquad (4)$$

where B is inhibition parameter for rate inhibition by succinic acid.
The equation (4) on rearrangement becomes

$$1/K_{inh} = 1/k_1 + B [\text{succinic acid}] / k_1 \qquad (5)$$

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.
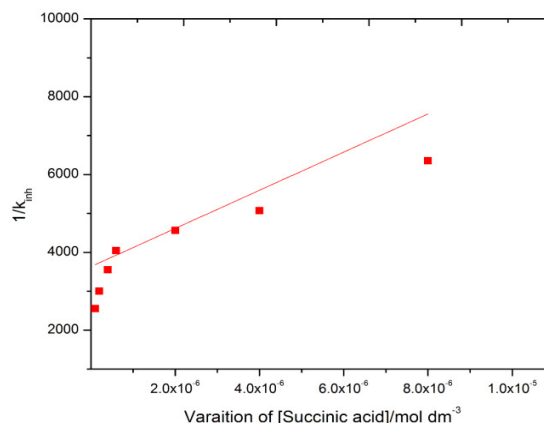

Fig. 2. Effect of succinic acid at [S(IV)] = 2 × 10⁻³ mol L⁻¹ and at 30°C, in phosphate buffered medium.

The values of intercepts($1/k_1$) and slope (B/k_1) were found to be 1.16×10^3s and 4.68×10^9mol⁻¹ Ls at pH = 7.80, and 30°C. From these values the value of inhibition parameter B was found to be 4.02×10^5 mol⁻¹ L.

E. Co₂O₃ -Catalyzed Reaction
At first the kinetics of Co₂O₃-catalyzed reaction in the absence of inhibitor was studied.

F. [S(IV)] Variation
[S(IV)] was varied from 1×10^{-3} to 10×10^{-3} mol L⁻¹ at two different but fixed [Co₂O₃] 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. [Co₂O₃] Variation
The effect of [Co₂O₃] on the rate was studied and the values of first order rate constants k_{cat}, for S(IV) - autoxidation was determined at different [Co₂O₃] 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 [Co₂O₃] at pH = 7.80 and t = 30°C.

Co₂O₃(g L⁻¹)	$10^3 k_{cat}$ s⁻¹
0.1	3.04
0.2	3.52
0.3	4.24
0.4	4.79
0.5	5.97

The nature of dependence of k_{cat} on [Co₂O₃] indicates the operation of a two term rate law.

$$-d[S(IV)]/dt = k_{cat} [S(IV)] = k_1 + k_2 [Co_2O_3] [S(IV)] \qquad (6)$$
$$K_{cat} = k_1 + k_2 [Co_2O_3] \qquad (7)$$

The values of intercept is equal to k_1 and slope is equal to k_2 were found to be 7.1 s and 4.1 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 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 = 30°C.

$[S(IV)]$molL^{-1}	$[Co_2O_3]$ g L^{-1}	[Succinic acid] molL^{-1}	pH	Temperature	$10^4 k_{cat} k_1 + k_2[Co_2O_3]$
0.002	0.2	0.0002 M	7.80	30°C	1.82
0.002	0.2	0.0002 M	8.50	30°C	1.92
0.002	0.2	0.0002 M	8.90	30°C	1.86
0.002	0.2	0.0002 M	9.40	30°C	1.92

I. Rate Law in the Presence of succinic acid

A detailed study of dependence of rate on $[S(IV)]$, $[Co_2O_3]$, and pH in the presence of succinic acid revealed that the kinetics remain first order both in $[S(IV)]$ and $[Co_2O_3]$ and independent of pH obeys the following rate law.

-d $[S(IV)]$/dt = $(k_1 + k_2 [Co_2O_3] [S(IV)])/1 + B$ [succinic acid] (8)

k_{inh} = $(k_1 + k_2 [Co_2O_3]/1 + B)$ [succinic acid] = $k_{cat}/1 + B$ [succinic acid] (9)

$1/k_{inh}$ = $1 + B$ [succinic acid]/ k_{cat} (10)

$1/k_{inh}$ = $1/ k_{cat} + B$ [succinic acid]/ k_{cat} (11)

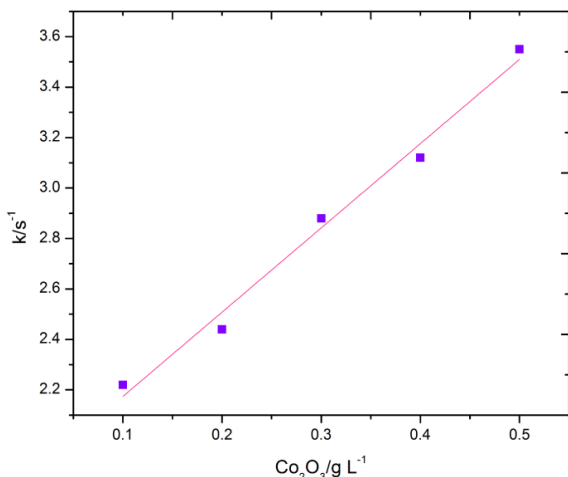A plot between $[Co_2O_3]$ v/s first order rate constant is linear (fig. 3) with intercept 2.53s^{-1} and slope 5.18 g^{-1} L s^{-1}.

Fig. 3. Effect of $[Co_2O_3]$ at succinic acid = 2×10^{-4} mol L^{-1}, pH=7.80 and at t = 30°C, in phosphate buffered medium.

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

[Succinic acid]	$10^4 k_{inh}$ s^{-1}	$1/k_{inh}$ s
1×10^{-7}	9.20	1087.0
2×10^{-7}	8.29	1206.3
4×10^{-7}	6.83	1466.3
2×10^{-6}	5.94	1686.3
4×10^{-6}	4.73	2118.6
6×10^{-6}	3.29	3048.8
1×10^{-5}	2.42	4149.4

A plot between $1/K_{inh}$v/s [succinic acid] is linear, with intercept = 1.37×10^3s and slope = 2.84×10^8mol^{-1} L s from which the value of B = 2.05×10^4mol^{-1} L.
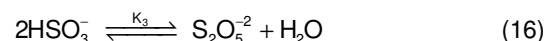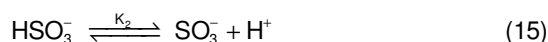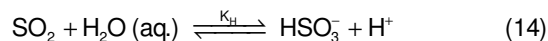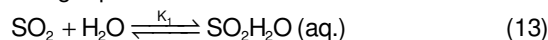
J. Effect of temperature

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 60.99 kJ mol^{-1}.

Table 4: 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}, [succinic acid] = 2×10^{-4} mol L^{-1}, t = 30°C, and pH = 7.80.

t °C	$10^4 k_{obs}$,s^{-1}
30	3.48
35	5.34
40	7.36

V. 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.

$$SO_2 + H_2O \underset{K_1}{\rightleftharpoons} SO_2H_2O \text{ (aq.)} \qquad (13)$$

$$SO_2 + H_2O \text{ (aq.)} \underset{K_H}{\rightleftharpoons} HSO_3^- + H^+ \qquad (14)$$

$$HSO_3^- \underset{K_2}{\rightleftharpoons} SO_3^- + H^+ \qquad (15)$$

$$2HSO_3^- \underset{K_3}{\rightleftharpoons} S_2O_5^{-2} + H_2O \qquad (16)$$

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.

$$Co_2O_3.SO_3^{-2} \underset{}{\overset{K_1}{\rightleftharpoons}} Co_2O_3.SO_3^{-2} \tag{17}$$

$$Co_2O_3.SO_3^{-2} + O_2 \underset{}{\overset{K_2}{\rightleftharpoons}} Co_2O_3.SO_3^{-2}.O_2 \tag{18}$$

$$Co_2O_3.SO_3^{-2}.O_2 \overset{k_1}{\longrightarrow} Co_2O_3. + SO_3^{-1} + O_2^{-1} \tag{19}$$

$$SO_3^{-1} + O_2 \overset{k_2}{\longrightarrow} SO_5 \tag{20}$$

$$SO_5 + SO_3^{-2} \overset{k_3}{\longrightarrow} SO_3 + SO_5^{-2} \tag{21}$$

$$SO_5^{\bullet} + SO_3^{-2} \overset{k_4}{\longrightarrow} SO_4 + SO_4^{-2} \tag{22}$$

$$SO_5^{-2} + SO_3^{-2} \overset{k_5}{\longrightarrow} 2SO_4^{-2} + SO_4^{-2} \tag{23}$$

$$SO_4^{\bullet} + SO_3^{-2} \overset{k_6}{\longrightarrow} SO_3 + SO_4^{-2} \tag{24}$$

$$SO_4^{\bullet} + x \overset{k_7}{\longrightarrow} \text{Non Chain product} \tag{25}$$

$$SO_4^{\bullet} + \text{succinic acid} \overset{k_8}{\longrightarrow} \text{Non Chain product} \tag{26}$$
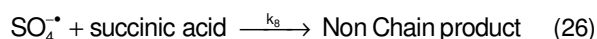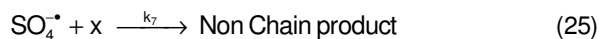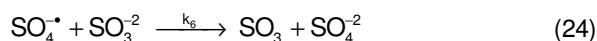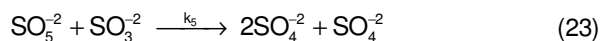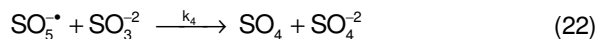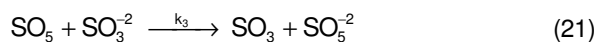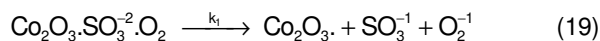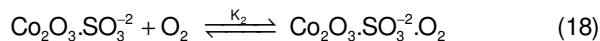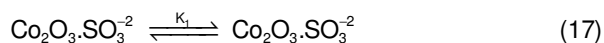
In alkaline medium the rate of Co_2O_3 catalysed reaction is highly decelerated by the addition of organics like that of reported by Husain *et al.,* [28-31] this indicates the operation of a radical mechanism involving oxysulphur free radicals, like SO_3^{-}, SO_4^{-} and SO_5^{-}. The inhibition is caused through the scavenging of SO_4^{-} by inhibitors such as ethanol and benzene, etc.

As reported by Begum *et al.,* [32] a radical mechanism operates in those reactions in which the inhibition parameter lies 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 succinic acid. Based on the observed results including the inhibition by succinic acid, the following radical mechanism is proposed which similar to that proposed by Sharma *et al.,* [33] in the acetic 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 $d[SO_3]/dt$, $d[SO_4]/dt$ and $d[SO_5]/dt$ to zero it can be shown that the rate of initiation is equal to the rate of termination.

$$k_1[Co_2O_3(SO_3^{-2})(O_2)] = \{k_7[X] + k_8[\text{Succinic acid}]\} [SO_4^{-1}] \tag{27}$$
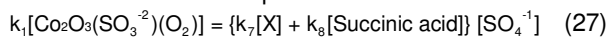
Since the reaction is completely stopped in the presence of [succinic acid] at 1×10^{-3}mol L^{-1}, so the steps (15) & (19) appear to be unimportant. The contribution of propagation reaction (18) been significant in the Co_2O_3 catalyzed. Reaction where the autoxidation reaction should have occurred even in the presence of high succinic acid concentration. But this is not true and the reaction is completed seized in the presence of high concentration of succinic acid. This led us to ignore the step (18) and assume only the rate of reaction given by equation (28).

$$R_{cat} = \frac{k_1 [Co_2O_3] [S(IV)]}{\{k_9[x] + k_{10}[\text{Succinic acid}]\}} \tag{28}$$

Sharma *et al* proposed a similar mechanism for the Ag (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 law we observe the similarity in these two. The calculated value of inhibition constant B is 3.17×10^5

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_2O_3 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_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.

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

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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