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Kinetics and Mechanism of Oxalic acid Inhibited and Heterogeneous Co_2O_3 Catalyzed Autoxidation of S(IV) in Atmospheric Water

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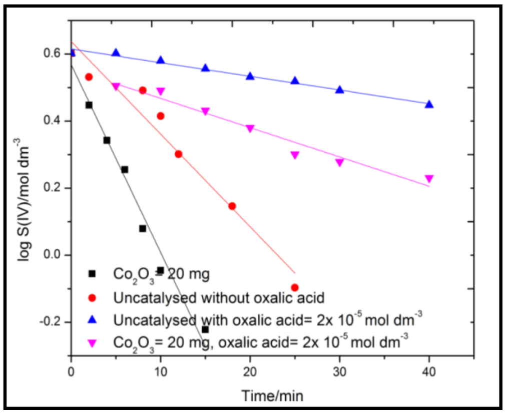
ABSTRACT

The kinetics of the oxalic acid inhibited Co_2O_3catalysed autoxidation of S(IV) in alkaline medium has been studied and based on the observed results following rate law and a free radical mechanism 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 determined to59.33 kJ mol^{-1}.The activation of energy was calculated by Arrhenius equation –d[S(IV)]/dt = (k_1+k_2 [Co_2O_3])[S(IV)/1 + B [Oxalic acid].

Graphical Abstract



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.

Keywords: Kinetics, Autoxidation; SO_2, Co_2O_3, Catalysis, Inhibition, Oxalic acid.

INTRODUCTION

The rapid industrial development on all fronts has let to several environmental pollution phenomena and the chemistry is at the back of all these. Of these, acid rain, stratospheric ozone depletion, green house effect and carbon monoxide pollution are the most prevalent. Here we are concerned mainly with the phenomenon of acid rain which is of common occurrence in several industrially developed countries in northern hemisphere [1]. In our own country, the level of SO_2 in atmospheric environment is increasing and, therefore, the danger of acid rain cannot be simply wished away. A large number of organic and inorganic chemical species are released in to the atmosphere by anthropogenic and natural sources [2].

The catalytic role of several metal oxides such as CoO [3], Co_2O_3 [4], Ni_2O3 [5], CuO [6], MnO_2 [7] and Cu_2O [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] ammonia [13], formic acid, isopropyl alcohol, isoamyl alcohol, aniline, benzamide, sodium benzoate [14-19], ascorbic acid [20], organic compounds [21], VOC [22], diesel truck particles [23].

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 oxalic acid on this reaction has been studied to know the nature of mechanism.

MATERIALS AND METHODS

The experimental procedure was exactly the same as described earlier by Prasad *et al* [24]. All calculations were performed in MS Excel.

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 [25].

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

$$S(IV) + 0.5\ O_2 \longrightarrow S(IV) \quad (1)$$

RESULTS AND DISCUSSION

Preliminary Investigation: The kinetics of both unanalyzed and Co_2O_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 fig. 1.

Unanalyzed 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 is in the range 1×10^{-3} mol dm^{-3} to 6×10^{-3} $moldm^{-3}$ 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)] versus 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).

$$-d\,[S(IV)/dt = [S(IV)] \quad (2)$$

[Oxalic acid] dependence: The major aim of this study was to examine the effect of organic inhibitors on the reaction rate, oxalic acid was chosen as the one organic compound. On increasing the concentration of oxalic acid from 5×10^{-5} to 5×10^{-4} $molL^{-1}$, the rate of reaction decreased.

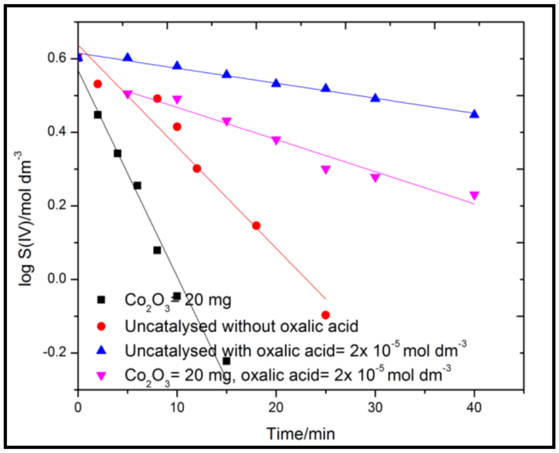


Figure 1. The disappearance of [S(IV)] with time in air-saturated suspensions at [S(IV)] = 2×10^{-3} molL^{-1}, at 30°C and pH = 7.80

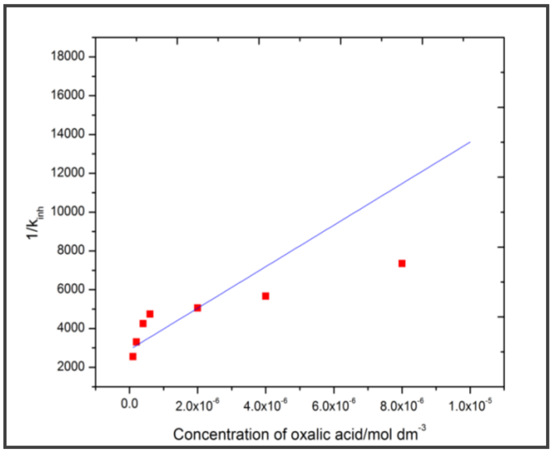


Figure 2. Effect of oxalic acid at [S(IV)] = 2 × 10^{-3} mol L^{-1} and at 30°C, in phosphate buffered medium

Table 1. The values of k_1 for unanalyzed 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

However, the nature of the [S(IV)]-dependence in presence of oxalic acid did not change and remained first order. The first order rate constant k_{inh}, were defined by rate law (3)

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

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

$$k_{inh} = k_1 / (1+B\,[\text{oxalic acid}])(4)$$

Where, B is inhibition parameter for rate inhibition by oxalic acid. The equation (4) on rearrangement becomes

$$1/ k_{inh} = 1/ k_1 + B\,[\text{oxalic acid}] / k_1\,(5)$$

In accordance with eq.(5) the plot of 1/ k_{inh} versus [oxalic 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 2.9×10^3 s and 1.08×10^9 mol^{-1}L s at pH = 7.80, and 30ºC. From these values the value of inhibition parameter B was found to be 2.68×10^5 mol^{-1}L.

Co_2O_3 -Catalyzed Reaction: At first the kinetics of Co_2O_3-catalyzed reaction in the absence of inhibitor was studied.

[S(IV)] Variation: The concentration of S(IV) was varied from 1×10^{-3} to 10×10^{-3} molL^{-1} at two different but fixed [Co_2O_3] 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.

$[Co_2O_3]$ 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=7.80, t=30°C. The results of k_{cat} 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	3.04
0.2	3.52
0.3	4.24
0.4	4.79
0.5	5.97

The nature of dependence of kcat on $[Co_2O_3]$ indicates the operation of a two term rate law.

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

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

The values of intercept is equal to k_1 and slope is equal to k_2 were found to be7.1 s and 4.1 $mol^{-1}Ls$, respectively at 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_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)]molL^{-1}	$[Co_2O_3]$ g L^{-1}	[oxalic acid] molL^{-1}	pH	temp.	$10^4 k_{cat}$ $k_1 + k_2[Co_2O_3]$
0.002	0.2	0.0002 M	7.80	30°C	2.67
0.002	0.2	0.0002 M	8.50	30°C	2.73
0.002	0.2	0.0002 M	8.90	30°C	2.52
0.002	0.2	0.0002 M	9.40	30°C	2.44

Rate Law in the Presence of oxalic acid: A detailed study of dependence of rate on [S(IV)], $[Co_2O_3]$ and pH on the reaction in the presence of oxalic acid 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 (Table 4).

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

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

$$1/\ k_{inh} = 1 + B\,[oxalic\ acid] / k_{cat} \quad (10)$$

$$1/\ k_{inh} = 1/k_{cat} + B\,[oxalic\ acid] / k_{cat} \quad (11)$$

A plot between $[Co_2O_3]$ versus first order rate constant is linear (fig. 3) with intercept 1.84 s^{-1} and slope 3.34 $g^{-1}L\ s^{-1}$.

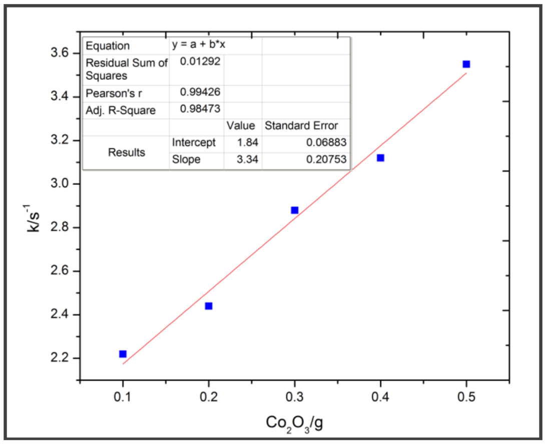


Figure 3. Effect of [Co_2O_3] at oxalic acid = 2×10^{-4} mol L^{-1} , pH=7.80 and at t = 30°C, in phosphate buffered medium.

Table 4. The variation of [oxalic 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

[oxalic acid]	$10^4 k_{inh}$ s^{-1}	$1/k_{inh}$ s
1×10^{-7}	4.87	205.45
2×10^{-7}	3.71	269.89
4×10^{-7}	3.12	320.98
6×10^{-7}	2.86	349.15
2×10^{-6}	2.18	458.81
4×10^{-6}	1.88	532.35
8×10^{-6}	1.36	735.07
1×10^{-5}	0.57	1740.36

A plot between $1/K_{inh}$ v/s [oxalic acid] is linear, with intercept = 2.08×10^2 s and slope = 1.21×10^8 mol^{-1} L s from which the value of B = 5.56×10^5 $mol^{-1}L$.

Effect of temperature: The values of k_{obs} were determined at three different temperatures in the range 30°C to 40°C**.** The results were given in table 5. These values yielded an apparent empirical energy of activation 17.4 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}, [oxalic acid] =2×10^{-4} mol L^{-1},t = 30°C, and pH =7.80.

t °C	10^4 k_{obs},s^{-1}
30	2.27
35	5.21
40	7.05

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.

$$SO_2 + H_2O \xrightleftharpoons{K_H} SO_2.H_2O(aq.) \quad (13)$$

$$SO_2.H_2O(aq.) \xrightleftharpoons{K_1} HSO_3^- + H^+ \quad (14)$$

$$HSO_3^- \xrightleftharpoons{K_2} SO_3^- + H^+ \quad (15)$$

$$2HSO_3^- \xrightleftharpoons{K_3} S_2O_5^{-2} + H_2O \quad (16)$$

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 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 (7.8-9.4), 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 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 present study, the dependence of oxygen is shows that the formation of surficial complex by adsorption of O_2 on the particle surface of Co_2O_3 through the fast step.

$$Co_2O_3 + SO_3^{-2} \xrightleftharpoons{K_1} Co_2O_3.SO_3^{-2} \quad (17)$$

$$Co_2O_3.SO_3^{-2} + O_2 \xrightleftharpoons{K_2} Co_2O_3.SO_3^{-2}.O_2 \quad (18)$$

$$Co_2O_3.SO_3^{-2}.O_2 \xrightarrow{k_1} Co_2O_3. + SO_3^{-1} + O_2^{-1} \quad (19)$$

$$SO_3^{-1} + O_2 \xrightarrow{k_2} SO_5 \quad (20)$$

$$SO_5 + SO_3^{-2} \xrightarrow{k_3} SO_3 + SO_5^{-2} \quad (21)$$

$$SO_5^{-\bullet} + SO_3^{-2} \xrightarrow{k_4} SO_4 + SO_4^{-2} \quad (22)$$

$$SO_5^{-2} + SO_3^{-2} \xrightarrow{k_5} 2SO_4^{-2} + SO_4^{-2} \quad (23)$$

$$SO_4^{-\bullet} + SO_3^{-2} \xrightarrow{k_6} SO_3 + SO_4^{-2} \quad (24)$$

$$SO_4^{-\bullet} + x \xrightarrow{k_7} \text{Non Chain product} \quad (25)$$

$$SO_4^{-\bullet} + \text{aniline} \xrightarrow{k_8} \text{Non Chain product .} \quad (26)$$

In alkaline medium the rate of Co_2O_3 catalyzed reaction is highly decelerated by the addition of oxalic acid like that of ethanol reported by Gupta *et al* [26] this indicates the operation of a radical mechanism involving oxysulphur free radicals, like SO_3^-, SO_4^- and SO_5^- [27]. The inhibition is caused through the scavenging of SO_4^- by inhibitors such as ethanol and benzene, etc.

As reported by Sameena*et al* [28] 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. The Co_2O_{3}-catalyzed reaction in presence of oxalic acid. Based on the observed results including the inhibition by oxalic acid, the following radical mechanism is proposed which similar to that proposed by Mudgal *et al* [29] in the ethanol inhibition of the CoO catalyzed reaction.

In the mechanism, no role is assigned to $O2^-$, 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.

$$k_1[Co_2O_3(SO_3^{2-})(O_2)]=\{k_7[X]+k_8[\text{oxalic acid}]\}[SO_4^-] \quad (27)$$

Since the reaction is completely stopped in the presence of [oxalic acid] at 1 x 10^{-3}mol L^{-1}, so the steps (15) and (19) appear to be unimportant. The contribution of propagation reaction (18) been significant in the Co_2O_3 catalyzed. The autoxidation reaction should have occurred even in the presence of high oxalic acid concentration. But this is not true and the reaction is completed seized in the presence of high concentration of oxalic acid. This led us to ignore the step (18) and assume only the rate of reaction given by equation (28).

$$R_{cat} = \frac{k^1 [Co_2O_3] [S(IV)]}{\{1 + k_1[s(IV)] \{k_7 [x] + k_8 [oxalic acid]\}} \quad (28)$$

Manoj*et al* [30] proposed a similar mechanism for the CoO catalyzed autoxidation of sulfur dioxide inhibited by ethanol, which lead to the same rate law. By comparing derived rate law with the experimental rate law we observe the similarity in these two [31-33]. The calculated value of inhibition constant B is 2.68×10^5 $mol^{-1}L$ which is in the range of 10^3 to 10^5. So on the base of calculated value of B, we concluded that oxalic acid act as a free radical scavenger in the Co_2O_3 catalyzed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can operate in this system [34-36].

APPLICATION

It is important in understanding the mechanism of the atmospheric oxidation of S(IV) by O_2.

CONCLUSION

The role of oxalic act as an inhibitor in Co_2O_3 catalyzed 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.

$$d[SIV)]/dt = (k_1 + k_2[Co_2O_3]) [S(lV)]/ 1 + B [oxalic acid]$$

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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