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RESEARCH ARTICLE

Co_2O_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_2O_3. Based on the observed results the following rate law is given and a free radical mechanism has been proposed. $-d[S(lV)]/dt = (k_1+k_2[Co_2O_3])\ [S(lV)]/1+B\ [benzamide]$. Experiments were carried out at $30 \leq T\ °C \leq 40$, $7.8 \leq pH \leq 9.4$, 1×10^{-3} mol/dm^3 $\leq [S(lV)] \leq 6 \times 10^{-3}$ mol/dm^3, 0.1 g/L $\leq [Co_2O_3] \leq$ 0.4g/L, 1×10^{-3}mol/dm^3 $\leq$ [benzamide] $\leq 5\times10^{-3}$ 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_2O_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_2O_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_2O_3; Ni_2O_3; CuO; MnO_2 and Cu_2O; 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[19], alcohols[20], carboxylic acid[21], formic acid, isopropyl alcohol, isoamyl alcohol, aniline, benzamide, sodium benzoate[22-27], ascorbic acid[28], organic compounds[29], VOC[30] and diesel truck particles[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_2O_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[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 ^{o}C. The reactions were initiated by adding the desired volume of standard Na_2SO_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^3 of buffer made from Na_2HPO_4 (0.08 mol L^{-1}) and KH_2PO_4 (0.02 mol L^{-1}) for alkaline medium were used (total volume 100 m^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_2O_3 was filtered out and sulphate was estimated gravimetrically by precipitating sulphate ions as $BaSO_4$ using standard procedure[33].

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

$$S(IV) + 0.5O_2 \longrightarrow S(VI) \tag{1}$$

Results and Discussion

Preliminary investigation

The kinetics of both uncatalysed 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 Figure 1.

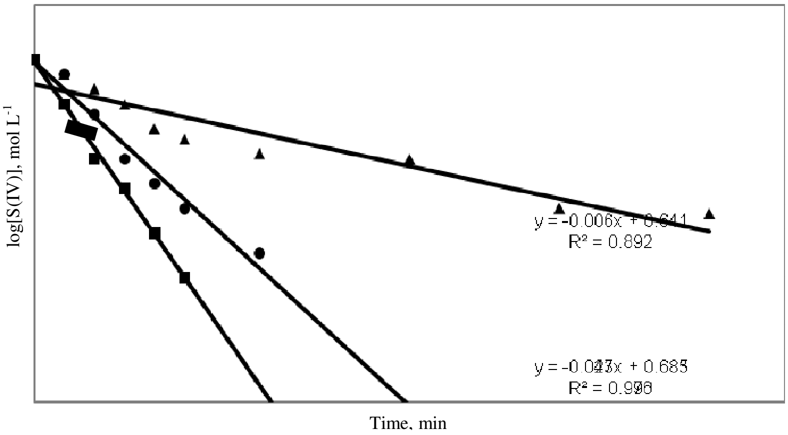

Figure 1. The disappearance of [S(IV)] with time in air – saturated suspensions at [S(IV)] = 2×10^{-3} mol dm^{-3},at 30 °C and pH = 7.88, (■) Co_2O_3 = 20 mg, benzamide = 0 mL, (●) uncatalysed and without benzamide (▲) Co_2O_3 = 20 mg , benzamide = 5×10^{-3} mol dm^{-3}

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 is 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.

$$-d\,[S(IV)]\,/dt = k_1\,[S(IV)] \tag{2}$$

Table 1. Values of k_1 for uncatalysed reaction at different [S(IV)] at pH= 7.34 and T = 30 °C

[S(IV)] mol dm^{-3}	$10^4 k_1$ s^{-1}
0.001	10.5
0.002	10.6
0.004	10.1
0.006	10.5

[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.

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

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

$$k_{inh} = k_1 /(1+B[Benzamide \tag{4}$$

Where B is inhibition parameter for rate inhibition by benzamide.

The Eq. 4 on rearrangement becomes

$$1/ k_{inh}=1/ k_1 +B[\text{Benzamide}]/ k_1 \qquad (5)$$

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

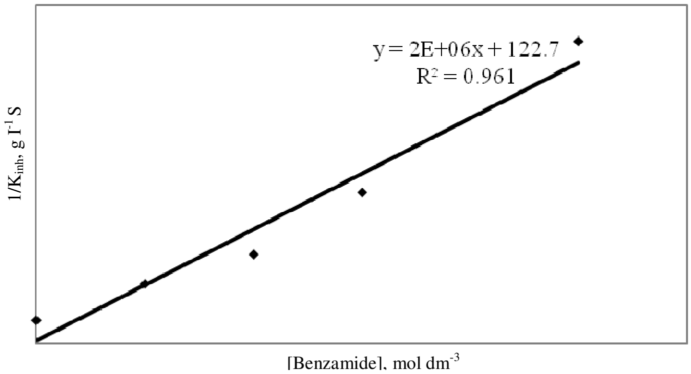

Figure 2. Effect of benzamide at [S(IV)] = 2×10^{-3} mol dm^{-3} and at 30 °C in phosphate buffered medium

Co_2O_3 Catalyzed reaction

At first the kinetics of Co_2O_3 catalyzed reaction in the absence of benzamide was studied.

[S(IV)] Variation

The concentration of S(IV) was varied from 1×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3}at two different but fixed [Co_2O_3] of 0.1 and 0.2 g L^{-1} was carried outat pH = 7.34 and T=30 °C. The kinetics was found to pseudo- first order in both cases.

[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=7.34, T=30 °C. The results are given in Table 2.

Table 2. The value of k_{cat} at different [Co_2O_3] at pH = 7.80 and T = 30 ºC

Co_2O_3, g L^{-1}	$10^3\,k_{cat}$ s^{-1}
0.1	8.8
0.2	13.7
0.3	16.9
0.4	21.8

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

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

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

The values of intercept is equal to k_1 and slope is equal to k_2 were found to be 5.1×10^{-4} s and 4.01×10^{-3} mol^{-1} dm^{-3} 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 [buffer] was examined by varying the concentration of both Na_2HPO_4 and KH_2PO_4 in such a way that the ratio $[Na_2HPO_4]$ / $[KH_2PO_4]$ 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 $[Co_2O_3] = 0.2$ g L^{-1}, [S(IV) = 2×10^{-3} mol dm^{-3} and T = 30 °C

[S(IV)] mol dm^{-3}	$[Co_2O_3]$ g L^{-1}	[Benzamide] mol dm^{-3}	pH	Temp. °C	10^4 k_{cat} $k_1 + k_2[Co_2O_3]$
0.002	0.2	0.003 M	7.90	30 °C	5.07
0.002	0.2	0.003 M	8.15	"	5.22
0.002	0.2	0.003 M	8.55	"	5.24
0.002	0.2	0.003 M	9.45	"	5.09

Rate law in the presence of benzamide

A detailed study of dependence of rate on [S(IV)], $[Co_2O_3]$ and pH on the reaction in the presence of benzamide 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.

By increasing the sodium benzoate concentration the rate decelerates *i.e.*, inhibition occurs. The results are shown in Table 4 and the effect of $[Co_2O_3]$ 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.

$$-d\,[S(IV)]\,/dt = (k_1+k_2[Ag(I)]\,[S(IV)]\,/\,1 + B\,[\text{Benzamide}], \tag{8}$$

Where,

$$k_{inh} = (k_1+k_2[Ag(I)]\,/\,1 + B\,[\text{Benzamide}] = k_{cat}/\,1 + B\,[\text{Benzamide}] \tag{9}$$

$$1/\ k_{inh} = 1 + B\,[\text{Benzamide}]\ /\,k_{cat}, \tag{10}$$

$$1/\ k_{inh} = 1/\,k_{cat} + B\ [\text{Benzamide}]\,/\ k_{cat}. \tag{11}$$

A plot between $[Co_2O_3]$ *vs.* first order rate constant is linear Figure 3 with intercept 1.65×10^{-4} s^{-1} and slope 6.21×10^{-4} g^{-1} L s^{-1}.

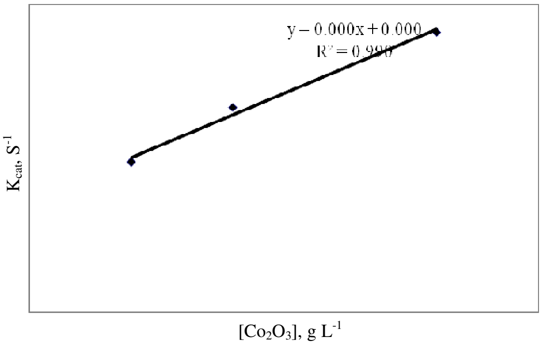

Figure 3. Effect of [S(lV)] at benzamide = 3×10^{-3} g L^{-1}, pH=7.34 and at 30 °C, in phosphate buffered medium

A plot between $1/k_{inh}$ *vs.* [benzamide] is linear with intercept = 6.83×10^2 s and slope = 1.05×10^6 mol^{-1} dm^{-3} s from which the value of B = 1.5×10^3 $mol^{-1}dm^{-3}$

Table 4. The variation of [benzamide] at [S(IV)] = 2×10^{-3} mol dm^{-3}, [Co_2O_3] = 0.1 g L^{-1}, T = 30 °C and pH = 7.34

[Benzamide]	k_{inh}	$1/k_{inh}$
0	10.1×10^{-4}	990
1×10^{-3}	5.7×10^{-4}	1754
2×10^{-3}	4.06×10^{-4}	2439
3×10^{-3}	2.79×10^{-4}	3571
5×10^{-3}	1.63×10^{-4}	6250

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} air saturated suspensions at [S(IV)] = 2×10^{-3} mol dm^{-3}, [Co_2O_3] = 0.2 g L^{-1}, [benzamide] =3×10^{-3} mol dm^{-3}, T = 30 °C and pH = 7.34

T °C	$10^4 k_{obs}$ s^{-1}
30	5.07
35	6.62
40	8.47

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.

$$SO_2(g) + H_2O \overset{K_H}{\rightleftharpoons} SO_2.H_2O(aq.) \quad (12)$$

$$SO_2.H_2O(aq.) \overset{K_1}{\rightleftharpoons} HSO_3^{-1} + H^+ \quad (13)$$

$$HSO_3^{-1} \overset{K_2}{\rightleftharpoons} H^+ + SO_3^{-2} \quad (14)$$

$$2HSO_3^{-1} \overset{K_3}{\rightleftharpoons} H_2O + S_2O_5^{-2} \quad (15)$$

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 ºC 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 (7.9-9.4), 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[34] 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.,*[35] 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 Sharma[36] and Mudgal[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 2.46×10^3, which lies in the same range. This strongly supports the radical mechanism for the Co_2O_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 *et al.,*[38] Sharma *et al.,*[39-41] Sameena *et al.,*[42] in the ethanol inhibition of the CoO catalyzed reaction.

$$Co_2O_3 + SO_3^{2-} \underset{}{\overset{K_1}{\rightleftharpoons}} Co_2O_3.\ SO_3^{2-} \tag{16}$$

$$Co_2O_3.SO_3^{2-} + O_2 \overset{K_2}{\rightleftharpoons} Co_2O_3.SO_3^{2-}\ .\ O_2 \tag{17}$$

$$Co_2O_3.\ SO_3^{2-}.O_2 \xrightarrow{k_1} Co_2O_3 + \ SO_3^- + O_2^- \tag{18}$$

$$SO_3^- + O_2 \xrightarrow{k_2} SO_5^- \tag{19}$$

$$SO_5^- + SO_3^{2-} \xrightarrow{k_3} SO_5^{2-} + SO_3^- \tag{20}$$

$$SO_5^- + SO_3^{2-} \xrightarrow{k_4} SO_4^- + SO_4^{2-} \tag{21}$$

$$SO_5^{2-} + SO_3^{2-} \xrightarrow{k_5} 2SO_4^{2-} \tag{22}$$

$$SO_4^- + SO_3^{2-} \xrightarrow{k_6} SO_4^{2-} + SO_3^- \tag{23}$$

$$SO_4^- + x \xrightarrow{k_7} \text{Nonchain product} \tag{24}$$

$$SO_4^- + \text{benzamide} \xrightarrow{k_8} \text{Nonchain product} \tag{25}$$

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_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. (Eq. 26)

$$k_1[Co_2O_3(SO_3^{2-})(O_2)]=\{k_7[X]+k_8[\text{benzamide}]\}[SO_4^-] \tag{26}$$

Since the reaction is completely stopped in the presence of [benzamide] at $1.2\text{x}10^{-2}$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_2O_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).

$$-d[S(IV)]/dt = R_{cat} = k_6\,[SO_4^-]\,[SO_3^{2-}] \tag{27}$$

By substituting the value of (SO_4^-) we get

$$R_{cat} = \frac{k_6k_1[Co_2O_3.SO_3^{2-}.O_2][SO_3^{2-}]}{k_7[x]+k_8[\text{benzamide}]} \tag{28}$$

From equilibrium Eq. 13 and Eq. 14

$$R_{cat} = \frac{k_6 K_2\ K_1\,[Co_2O_3][S(IV)][O_2]}{\{1 + k_1[s(IV)]\{k_7\,[x] + k_8\,[benzamide]\}} \tag{29}$$

At fixed O_2, replacing $k_6\,k_1\,k_2[O_2]$ by k^1 we get

$$R_{cat} = \frac{k^1\,[Co_2O_3][S(IV)]}{\{1 + k_1[s(IV)]\{k_7\,[x] + k_8\,[benzamide]\}} \tag{30}$$

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

$$R_{cat} = \frac{k^1\,[Co_2O_3][S(IV)]}{k_7\,[x] + k_8\,[benzamide]} \tag{31}$$

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 1.5×10^3 mol^{-1} 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 Co_2O_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 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.

$$-d[S(lV)]/dt = (k_1 + k_2[Co_2O_3])\,[S(lV)]/1 + B\,[Benzamide]$$

Based on the experimental results, rate constants and orders of the reactions were determined. The reaction order in SO_2 was pseudo- first order for both reactions in the presence and absence of benzamide. The effect of pH on SO_2 oxidation in the presence of Co_2O_3 and benzamide has been studied and found rate of the SO_2 oxidation independent of the pH change during the reaction. The effect of temperature of the solution on SO_2 oxidation catalysed by Co_2O_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 SO_2 autoxidation. The values of inhibition factor (B) for both uncatalysed and Ag(I) catalysed autoxidation of SO_2 in the presence of benzamide are $1.89\text{x}10^4$ and $1.50\text{x}10^3$ 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 SO_2 so by using it in the atmosphere rain water acidity can be controlled.

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