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Rate studies of CoO catalysed autoxidation of S(IV) inhibited by methanol in alkaline medium

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Abstract

The influence of methanol on CoO catalysed S(IV) oxidation in alkaline medium was studied. The kinetics of atmospheric autoxidation of sulphur (IV) by CoO in the pH range 7.34-9.40 has been studied and based on the observed results a free radical mechanism is operative and a rate law has been proposed. Hence the results are useful for modeling rain water acidity and therefore a great use of meteorology and atmospheric chemistry.

$$d[S(IV)]/dt = (k_1 + k_2[CoO]) [S(IV)]/I + B [Methanol].$$

Keywords: Kinetics, autoxidation, SO₂, CoO, catalysis, inhibition, methanol, free radical mechanism, buffer medium, inhibitor parameter

Introduction

Atmospheric chemistry is the study of chemical processes occurring in the Earth's atmosphere. It explores the composition, reactions, and transformations of chemical species in the air, including pollutants, greenhouse gases, and naturally occurring compounds. Understanding atmospheric chemistry is crucial for elucidating air quality, climate change, and the interactions between the atmosphere and other environmental systems. Many types of studies have been done on the atmospheric oxidation of S (IV) in the recent past, in aerosols and in bulk aqueous phase. The trace metal Ions which are part of all atmospheric systems and are catalyzing the oxidation of aqueous SO₂ in to acid sulfate. In with the oxidation of S(IV) by transition metal ions and their role in catalyzing the dioxide-S(IV) systems [1-3]. The metal oxides, which are present in the Atmosphere are integral part of suspended particulate matter. The role of various metal oxides such as CoO [4]; CO₂O₃ [5]; Ni₂O₃ [6]; CuO [7]; MnO₂ [8]; and Cu₂O [9]; and MnO₂ [10] in acidic medium has been studied and given a two term rate law. Gupta [11] *et al.*, studied the inhibiting effect of alcohol on the CoO, CO₂O₃ and Ni₂O₃ catalysed autoxidation reaction in alkaline medium and proposed a radical mechanism. The effect of alcohols has been studied on several catalysed S(IV) autoxidation in the effect of silver (I) catalyzed autoxidation of S(IV) in acetate buffer medium [11-12]. To explain these results and inhibition effect of organic compounds, the radical mechanism involving SO₃, SO₄ and SO radicals was proposed [13]. Further experiments were conducted for finding reactivity of oxysulphur radicals with organics, which proved that these compounds react with SO₄ the reactions with SO₃ and SO₅ appeared to be quite slow and hence unimportant. The methanol inhibition of the uncatalysed autoxidation of HSO₃⁻ was investigated by Connick *et al.*, (1995) [14] to shed more light on a mechanism of initiation in the absence of transition metal ions. Connick and Zhang (1996) [15] showed that in the presence of manganous ions the inhibition by methanol is more complex than indicated by simply adding to the overall reaction mechanism the step by which sulphate radicals are scavenged. This led us to investigate the kinetics of sulfur (IV) autoxidation catalyzed by CoO in the pH range 7.34 - 9.40 and the effect of methanol has been studied in alkaline media to delineate the nature of the mechanism.

Experimental

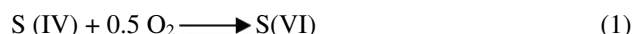
The experimental procedure was exactly the methodology described earlier by Prasad *et al.*, [16-18]. All chemical substances utilized were of analytical grade, and their solutions were prepared using double-distilled water. The reactions were carried out in 0.15-liter Erlenmeyer flasks, exposed to ambient air to facilitate the exchange of atmospheric oxygen. Each flask was situated within a beaker with an inlet at the lower part and an outlet at the upper part to enable the circulation of thermostatic water, maintaining the desired temperature at 33 ± 0.1 °C. The reaction were started by adding the desired volume of standard Na_2SO_3 solution for the reaction combination containing different added substances like buffer and catalyst oxide. The reaction mixture was continuously and magnetically stirred at 1600 ± 100 rpm to permit the part of atmospheric oxygen and to save the reaction from becoming oxygen mass exchange controlled. The kinetic studies were conducted in a buffered medium, maintaining a constant pH throughout the entire reaction process. For this purpose, a 10 cm^3 of buffer medium from of Na_2HPO_4 (0.08 mol dm^{-3}) and KH_2PO_4 (0.02 mol dm^{-3}) was used to create a basic alkaline medium with a total volume of 100 cm^3 , thus achieving the desired pH. The kinetic were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically in slightly alkaline medium as described earlier. The reproducibility of the

replicate measurements was generally better than compared to $\pm 10\%$. All calculations were conducted using MS Excel [19].

Product analysis

When the reaction was complete, the separation of CoO was accomplished through filtration and the determination of Sulphate was estimated gravimetrically. This involved the precipitation of sulfate ions as BaSO_4 , using standard procedure [20].

The product analysis showed the recovery of sulphate to be $98 \pm 2\%$, in all cases in agreement with eq. (1)



Results

Preliminary investigation

The kinetics of both uncatalysed and CoO Catalysed reaction were studied in alkaline medium in pH 7.34-9.40 and temperature 33 °C. In both of the cases, the first order dependence of S(IV) was observed in the kinetics data treatment for the determination of first order rate constant k_1 was calculated from $\log [\text{S(IV)}]$ versus time, t . The plots were shown in fig 1 it is observed that both the uncatalysed and CoO catalysed autoxidation of S (IV) reaction is inhibited by methanol.

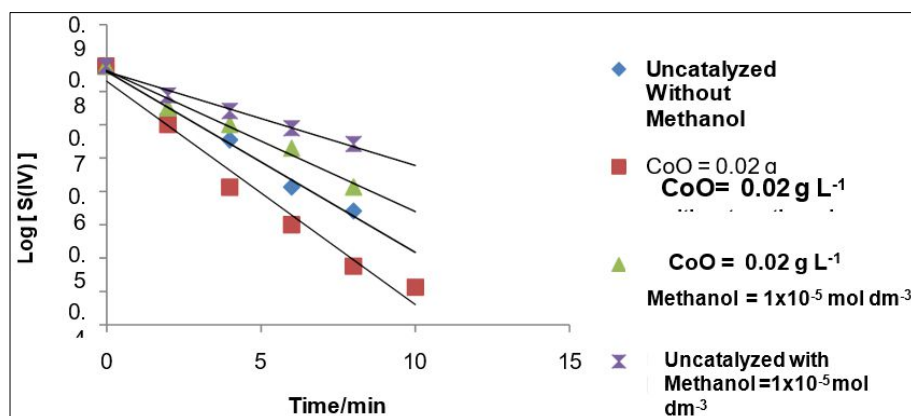


Fig 1: The disappearance of [S(IV)] with time in air saturated suspensions at $[\text{S(IV)}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at pH = 7.34, $t = 33$ °C

Uncatalysed reaction: In this study, the reaction was studied without the adding CoO.

Dependence of S (IV)

The detailed dependence of the reaction rate on [S(IV)] was studied by varying sulphite is the range of $1 \times 10^{-3} \text{ mol dm}^{-3}$ to $5 \times 10^{-3} \text{ mol dm}^{-3}$ at pH= 7.34, $t = 33$ °C in phosphate

buffer medium. The kinetics of [S(IV)] was found to be first order and are shown in Fig 1 and $\log [\text{S(IV)}]$ versus time plots were linear. The values of first order rate constant, k_1 are shown in table -1. The dependence of reaction rate on [S(IV)] follows the following rate law (2).

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

Table 1: The values of k_1 for uncatalysed reaction at different [S(IV)] at pH = 7.34, $t = 33$ °C $\text{Na}_2\text{HPO}_4 = 8 \times 10^{-2} \text{ mol L}^{-1}$ $\text{KH}_2\text{PO}_4 = 2 \times 10^{-2} \text{ mol L}^{-1}$

[S(IV)] mol dm^{-3}	(103) $k_1 \text{ s}^{-1}$
0.001	1.38
0.002	1.75
0.003	2.09
0.004	2.37
0.005	2.60

Dependence of methanol

To examine the effect of methanol inhibitor on the autoxidation of S(IV) in alkaline medium. Methanol was

varied from $1 \times 10^{-6} \text{ mol dm}^{-3}$ to $1 \times 10^{-4} \text{ mol dm}^{-3}$ and observed that the rate of the reaction decreased by increasing methanol. The results are given in Table 2.

The nature of the $[S(IV)]$ dependence in presence of methanol did not change and remains first order. The first order rate constant k_{inh} , in the presence of methanol was defined by rate law (3)

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

The value of first order rate constant k_{inh} in the presence of methanol decreased with increasing [Methanol] in agreement with the rate law.

$$k_{inh} = k_1/(1+B[Methanol]) \quad (4)$$

Where B is inhibition parameter for rate inhibition the equation (4) on rearrangement becomes

$$1/k_{inh} = 1/k_1 + B[Methanol]/k_1 \quad (5)$$

In accordance with the equation (5) the plot of $1/k_{inh}$ v/s [Methanol] was found to be linear with positive intercept fig 2. The values of intercept ($1/k_1$) and slope (B/k_1) were found to be 8.61×10^2 s and $2.1 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$ s at pH = 7.34, $t = 33^\circ\text{C}$ from these values the value of inhibition parameter B was found to be $2.5 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$

The values of k_{inh} at different [Methanol] are given in table 2

Table 2: The values of k_{inh} at different [Methanol] at pH = 7.34, $t = 33^\circ\text{C}$, $\text{Na}_2\text{HPO}_4 = 8 \times 10^{-2} \text{ mol L}^{-1}$ $\text{KH}_2\text{PO}_4 = 2 \times 10^{-2} \text{ mol L}^{-1}$

[Methanol] mol dm^{-3}	103 $k_{methanol}$ s $^{-1}$	1/ $k_{methanol}$ s
1×10^{-6}	1.23	813
3×10^{-6}	1.21	826
6×10^{-6}	1.13	884
8×10^{-6}	1.09	917
1×10^{-5}	1.08	925
3×10^{-5}	1.05	952
6×10^{-5}	1.01	990
8×10^{-5}	1.00	1000
1×10^{-4}	0.91	1098

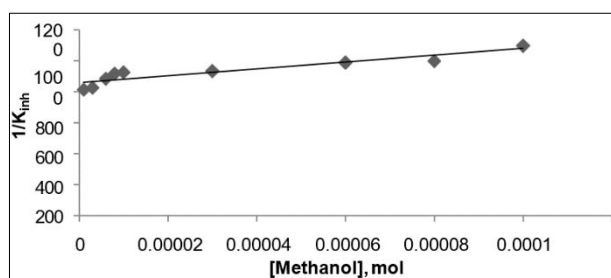


Fig 2: Effect of methanol at $[S(IV)] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ pH=7.34 and temp= 33°C in alkaline buffer medium

CoO catalysed reaction

The kinetics of CoO Catalysed autoxidation of S(IV) was studied in alkaline medium without inhibitor methanol.

[S(IV)] variation

The dependence of S(IV) on reaction rate was studied by varying $[S(IV)]$ from $1 \times 10^{-3} \text{ mol dm}^{-3}$ to $5 \times 10^{-3} \text{ mol dm}^{-3}$ at two different but fixed [CoO] of 0.01 and 0.02 g dm^{-3} at pH = 7.34, $t = 33^\circ\text{C}$ The kinetics was found to be first order and $[S(IV)]$ v/s time plots were linear as shown in Fig 1.

CoO variations: The effect of CoO on the reaction rate was studied by varying CoO from 0.01 to 0.05 gm dm^{-3} at

$S(IV) = 3 \times 10^{-3} \text{ mol dm}^{-3}$ pH=7.34, $t = 33^\circ\text{C}$ in alkaline medium. The values of first order rate constant k_{cat} given in Table 3 were plotted against [CoO] and are shown in fig 3. The nature of dependence of k_{cat} on CoO was indicated as two term rate law (6).

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

$$\text{Or } k_{cat} = k_1 + k_2[CoO] \quad (7)$$

From the plot in fig. 3 the values of intercept is equal to k_1 and slope is equal to k_2 were found to be 4.6×10^2 s and $1.7 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ s at pH = 7.34, $t = 33^\circ\text{C}$, in alkaline buffer medium.

Table 3: The value of k_{cat} at different [CoO] at pH = 7.34 and Temp. = 33°C , $\text{Na}_2\text{HPO}_4 = 8 \times 10^{-2} \text{ mol L}^{-1}$ $\text{KH}_2\text{PO}_4 = 2 \times 10^{-2} \text{ mol L}^{-1}$

CoO(g dm^{-3})	103 k_{cat} s $^{-1}$
0.01	2.20
0.02	2.31
0.03	2.45
0.04	2.54
0.05	2.60

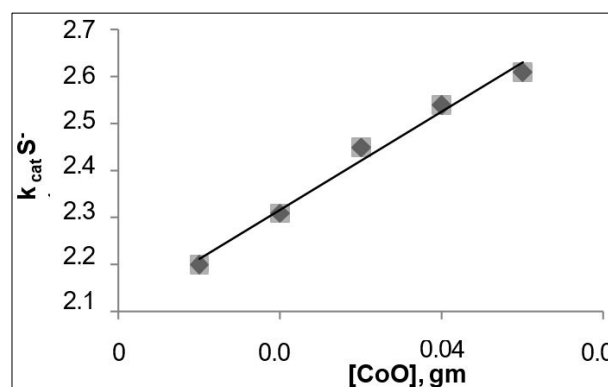


Fig 3: The dependence of catalyst concentration at $[S(IV)] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ pH = 7.34, $t = 33^\circ\text{C}$, in alkaline buffered medium

Variation of pH: pH variation was carried out within the range of 7.34 to 9.40, at fixed concentrations of S(IV), CoO, and methanol, temperatures. The results shows that the rate of reaction is independent of pH. Table-4. The effect of [buffer] was examined by varying the concentration of both Na_2HPO_4 & KH_2PO_4 so that the ratio $[\text{Na}_2\text{HPO}_4]/[\text{KH}_2\text{PO}_4]$ remained same, so pH remained fixed. The values showed that the rate of reaction to be insensitive to the buffer concentration. The results are given table-3

Table 4: Effect of pH at $[S(IV)] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at CoO, = 0.02 gm dm^{-3} , $t = 33^\circ\text{C}$ [Methanol] = $1 \times 10^{-5} \text{ mol dm}^{-3}$ $\text{Na}_2\text{HPO}_4 = 8 \times 10^{-2} \text{ mol L}^{-1}$ $\text{KH}_2\text{PO}_4 = 2 \times 10^{-2} \text{ mol L}^{-1}$.

PH	103 $k_{methanol}$ S $^{-1}$
7.34	1.63
8.50	1.49
8.90	1.80
9.40	1.77

Rate law in the presence of organics

A detailed study of dependence of rate on S(IV), [CoO] and pH with in the presence of methanol revealed that the kinetics remain first order both in S(IV) and [CoO] and independent of pH, Table-5 obeys the following rate law.

$$-d[S(IV)]/dt = (k_1 + k_2[CoO] [S(IV)] / 1 + B \text{ (Methanol)}) \quad (8)$$

$$\text{Where } k_{inh} = (k_1 + k_2[C \text{ oO}] / 1 + B \text{ (F.A)}) = k_{cat} / 1 + B \text{ (Methanol)} \quad (9)$$

$$1/k_{inh} = 1 + B \text{ (Methanol)} / k_{cat} \quad (10)$$

$$1/k_{inh} = 1/k_{cat} + B \text{ (Methanol)} / k_{cat} \quad (11)$$

Table 5: The values of k_{inh} at different [Methanol] at $[S(IV)] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, $[CoO] = 0.02 \text{ gm dm}^{-3}$, $pH = 7.34$, $t = 33^\circ\text{C}$, $Na_2HPO_4 = 8 \times 10^{-2} \text{ mol L}^{-1}$, $KH_2PO_4 = 2 \times 10^{-2} \text{ mol L}^{-1}$.

[Methanol] mol dm ⁻³	103k _{methanol} s ⁻¹	1/k _{methanol} s
1x10 ⁻⁶	1.95	512
3x10 ⁻⁶	1.81	552
6x10 ⁻⁶	1.80	555
8x10 ⁻⁶	1.67	598
1x10 ⁻⁵	1.63	613
3x10 ⁻⁵	1.60	625
6x10 ⁻⁵	1.58	632
8x10 ⁻⁵	1.50	666
1x10 ⁻⁴	1.49	671

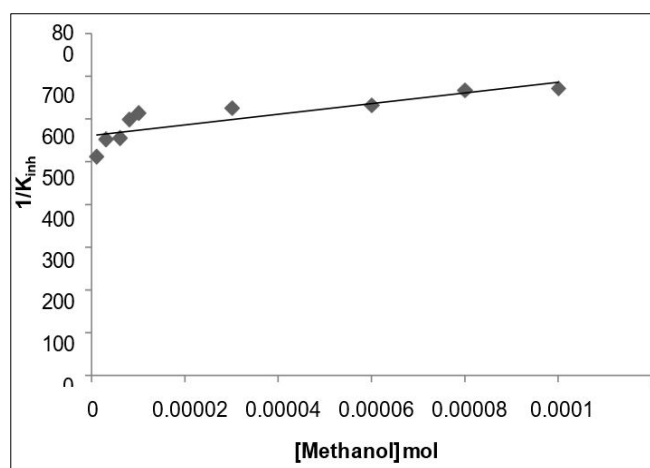


Fig 4: Effect of Methanol at $[S(IV)] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, $[CoO] = 0.02 \text{ gm dm}^{-3}$, $pH = 7.34$ and $temp = 33^\circ\text{C}$ in alkaline buffered medium

By plotting a graph between $1/k_{inh}$ versus [Methanol] gives a straight line with positive intercept fig. 4. The values of intercept = $1/k_{cat}$ and slope = B/k_{cat} from the graph these values are found to be $5.6 \times 10^2 \text{ s}$ and $1.2 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}$ respectively. From these values the value of inhibition parameter B can be determined, inhibition parameter $B = \text{slope/Intercept}$ that is $B = 2.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$.

Effect of temperature

The values of k_{obs} were determined at different temperatures in the range of 33°C to 48°C . The results are given in Table 6. By plotting a graph between $\log k$ v/s $1/T$ yield us an apparent empirical energy of activation $43.23 \text{ kJ mol}^{-1}$ in the presence of methanol.

Table 6: Effect of temperature at $[S(IV)] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at $[CoO] = 0.02 \text{ g dm}^{-3}$ [methanol] = $1 \times 10^{-5} \text{ mol dm}^{-3}$ $pH = 7.34$, $Na_2HPO_4 = 8 \times 10^{-2} \text{ mol L}^{-1}$, $KH_2PO_4 = 2 \times 10^{-2} \text{ mol L}^{-1}$.

t °C	103 k _{methanol} s ⁻¹
33 °C	1.63
38 °C	2.31
43 °C	2.99
48 °C	3.56

Discussion

In aqueous solution SO_2 is present in four forms $SO_2 \cdot H_2O$, HSO_3^{-1} , SO_3^{-2} , $S_2O_3^{-2}$ governed by the following equations.



In the range of pH (7.34- 9.40), S(IV) would generally be present as SO_3^{2-} . Since the reaction rate of under study not dependent on pH, we have considered that only SO_3^{2-} species to be reactive. In some modifications the autoxidation reactions of sulfur (IV) take place in the heterogeneous aqueous phase catalysed by a metallic oxide the development of surface complexes through the adsorption of sulfur (IV) and O_2 on the surface of the molecule and oxidation. Sulfur(IV) proposed oxidation states. In the heterogeneous reaction in strong liquid state of MnO_2 and S(IV), Halperin and Taube^[21] reported that the sulfite particles bind to the outside of the strong MnO_2 through the oxygen molecule. In the current study, the oxygen dependence shows that the arrangement of the surface complex proceeds rapidly through the adsorption of O_2 to the surface of the CoO molecule.

Bigelow *et al.*, (1898)^[22] studied the influence of alcohols such as ethanol, propanol and butanol on the reaction between sodium sulfite and O_2 and found that these alcohols limited the reaction rate. Backstrom (1929)^[23] also studied the inhibiting effect of aliphatic alcohols (ethanol, isopropanol, secondary butanol, benzyl alcohol) on the autoxidation of sodium sulfite in a soluble medium (initial pH 8.4). Backstrom (1934)^[24] proposed a mechanism to prevent a highly inhibitory oxidation reaction in the chain between sodium sulfite and oxygen. Connick and Zhang (1996)^[25] reported that when Mn^{+2} particles are considered, methanol inhibition is more unpredictable. Grgic *et al.*, (1998)^[26] examined the inhibition influence of oxalate, acetic acid and formate on the Fe-catalyzed autoxidation of S(IV) at estimated pH values of 2.8, 3.7 and 4.5 and found that oxalate it has a strong inhibiting effect on the reaction rate due to reduced measurement of the chemically dynamic Fe (III) particle complexation with oxalate.

Bostjan Podkrajsek *et al.*, (2006)^[27] investigated the influence of carboxylic acids on the Mn (II) catalyzed oxidation of sulfur (IV) and found that mono carboxylic acids inhibit oxidation and the more influence of caused formic acids.

In alkaline medium, the rate of the reaction catalysed by CoO is exceptionally slowed by the addition of formic acid, such as that of ethanol, reported by Gupta *et al.*^[28]. This shows the activity of a radical mechanism that includes oxy-sulfur-free radicals, such as $SO_3^- \cdot$, $SO_4^- \cdot$ and $SO_5^- \cdot$ ^[28, 29, 30]. The inhibition is caused by the interception of $SO_4^- \cdot$ by inhibitors such as ethanol and benzene, etc. Gupta *et al.*^[28] a radical mechanism operate has been reported to

work on reaction where the value of inhibition parameter is between 103 and 104. In the current study, the inhibition parameter is found to be $2.5 \times 10^3 \text{ mol dm}^{-3}$, which lies within a similar range. Based on the observed results,

including the inhibition by formic acids, the following radical mechanism is proposed which similar to that proposed by Gupta *et al.* in the ethanol inhibition of the CoO catalyst reaction^[31-33].



By assuming long chain hypothesis and steady state approximation $d[\text{SO}_3^{\cdot-}]/dt$, $d[\text{SO}_4^{\cdot-}]/dt$ and $d[\text{SO}_5^{\cdot-}]/dt$ to zero it can be shown that the rate of initiation is equal to the rate of termination. (Eq. 26)

$$k_1[\text{CoO}(\text{SO}_3^{2-})(\text{O}_2)] = \{k_7[\text{X}] + k_8[\text{Methanol}]\}[\text{SO}_4^{\cdot-}] \quad (26)$$

Since the reaction is completely stopped in the presence of methanol at $1 \times 10^{-4} \text{ mol dm}^{-3}$, So the steps (18) and (22) appear to be unimportant. The step (23) is ignored because the reaction is completely seized in the presence of higher concentration of methanol by omission and substitution from the above mechanism the following rate law can be obtain (27).

$$R_{\text{cat}} = k_1 [\text{CoO}][\text{S(IV)}] / k_7[\text{X}] + k_8 [\text{Methanol}] \quad (27)$$

Prasad *et al.* and Gupta *et al.*^[28] proposed a similar mechanism for the CoO catalysed autoxidation of sulfur dioxide inhibited by ethanol, which leads to the same rate law. By comparing the derived rate law with the experimental rate law, we observe the similarity in these two. The calculated value of inhibition parameter B is $2.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$. Which is in the range of 10^3 to 10^4 . So on the basis of calculated value of B. We concluded that methanol act as a free radical scavenger in the CoO catalysed autoxidation of aqueous sulfur dioxide in alkaline medium and a free radical mechanism can work in this mechanism.

Conclusion

The following conclusions are deduced from the results of the methanol inhibited CoO catalysed autoxidation of S(IV)

was that methanol inhibits the oxidation of S(IV) with the fast influence. The value of Inhibition factor of both uncatalysed and CoO catalysed autoxidation of S(IV) in the present study are in the range of 10^3 - 10^5 which shows that free radical mechanism is operative in this case also.

Environmental importance

Organics are able to inhibit the oxidation of SO_2 so rain water acidity can be controlled. They increase the life span of SO_2 so vegetation, national buildings, monuments, fishes of water bodies and human being are not affected by rain water acidity. 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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