Kinetics Of Formic Acid Inhibited Uncatalysed And CoO Catalyzed Autoxidation Of S(IV) In Alkaline Medium

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ABSTRACT:-

The kinetics of the formic acid inhibited CoO 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 calculated by Arrhenius equation. On the basis of inhibition parameters, the reaction follows free radical mechanism.

$$d[S(lV)]/dt \quad = \quad (k_1 + k_2[CoO]) [S(lV)]/1 + B [\text{Formic acid}]$$

KEYWORDS: Kinetics; Autoxidation; SO_2; CoO ; Catalysis; Inhibition ; formic acid, free radical mechanism

INTRODUCTION:-

The atmospheric oxidation of sulfur dioxide (SO_2) is a complex and dynamic process with significant implications for air quality, climate, and environmental health. In this, the kinetics of autoxidation reactions involving sulfur dioxide, particularly in alkaline media, have garnered attention due to their role in the formation of sulfate aerosols. The atmospheric reactions of SO_2 and NO_x etc. are major acid rain precursors and are responsible for acidification of various forms of atmospheric water[1]. Upon release into the atmosphere, SO_2 undergoes chemical transformations, including autoxidation reactions, driven by the presence of oxygen and other reactive species. These reactions play a crucial role in the formation of sulfate aerosols, which contribute to air quality issues and climate change. The catalytic role of several metal oxides such as CoO[2]; Co_2O_3[3]; Ni_2O_3[4]; CuO[5]; MnO_2[6] in acidic medium has been reported..The alkaline environment significantly influences the kinetics of sulfur dioxide autoxidation. Alkaline solutions are commonly found in atmospheric aerosols and aqueous droplets, making it essential to understand the kinetics of S(IV) oxidation under such conditions.

 In this, configuration of surficial complexes by adsorption of sulfur(IV) and O_2 on particle surface followed by subsequent oxidation of former by latter via a non-radical mechanism has been proposed. Herrmann et al(2000)[7] reported that the interaction between alcohols and SO_2 oxidation intermediates may have a bearing on acidity formation in the atmosphere. Alyea and Backstrom(1929)[8] studied the inhibiting effect of aliphatic alcohols on the oxidation of sodium sulphite in alkaline medium (pH 8.4). Later

Backstrom (1934)[9] proposed a radical mechanism for the autoxidation of S(IV) to show the probable contribution of radicals such as $SO_3^{-\bullet}$, $SO_4^{-\bullet}$ and $SO_5^{-\bullet}$ in the formation of a chain and to explain the alcohol inhibition. The S(IV) autoxidation reaction is known to proceed via both radical and non-radical mechanisms[10]. VOCs play a crucial role in tropospheric chemistry[11] 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[12-14]

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 CoO in the pH range 7.34-9.40 and so the effect of formic acid on this reaction has been studied to know the nature of mechanism.

EXPERIMENTAL

The experimental procedure was exactly the methodology described earlier by Prasad et al [15]. 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 $30\pm0.1^{o}C$.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 $moldm^{-3}$) and KH_2PO_4 (0.02 $moldm^{-3}$) 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 examples 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 compared to $\pm$ 10%. All calculations were conducted using MS Excel[16].

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 standared procedure[17]

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

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

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 $33^{o}C$. 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 [S(IV)] versus time, t. The plots were shown in fig 1 from the fig 1 it is observed that both the uncatalysed and CoO catalysed autoxidation of S (IV) reaction is inhibited by formic acid.
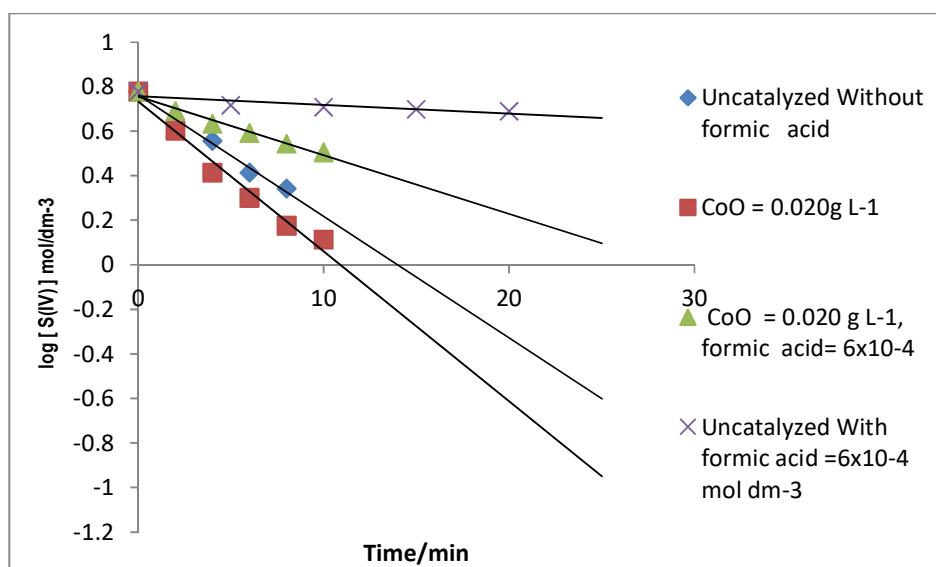
Fig.1 The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = $3x10^{-3}$ mol dm^{-3} at pH = 7.34, t = 33 ^{o}C

Uncatalysed Reaction

In this study, the reaction was examined without the adding CoO. An it is well known that the uncatalysed reaction is initiated by the presence of trace metal particle impurities in the reagent samples and in the distilled water utilized for the preparation of solution.

Dependence of S (IV)

The detailed dependence of the reaction rate on [S(IV)] was studied by varying sulphite is the range of $1×10^{-3}$ mol dm^{-3} to $5×10^{-3}$ mol dm^{-3} at pH= 7.34, t = 33°C in phosphate buffer medium. The kinetic was found to be first order in [S(IV)] as shown in Fig 1 and log [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).

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

Table 1-The values of k_1 for uncatalysed reaction at different [S(IV)] at pH =7.34, t=33°C, Na_2HPO_4 =$8x10^{-2}$ $molL^{-1}$, KH_2PO_4 = $2x10^{-2}$ mol L^{-1}

[S(IV)] mol dm^{-3}	$(10^3)\ k_1\ s^{-1}$
0.001	1.38
0.002	1.75
0.003	2.09
0.004	2.37
0.005	2.60

[Formic acid] Dependence

The aim of the study was to examine the effect of formic acid inhibitors on the autoxidation of S(IV) in alkaline medium so for this purpose formic acid was selected as the inhibitor and varying the [formic acid] from $3x10^{-5}$ mol dm^{-3} to $8x10^{-4}$ mol dm^{-3} we observed the rate of the reaction decreased by increasing formic acid. The results are given in Table 2.

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

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

The values of $k_{inh\,at}$ different [formic acid] are given in table 2

Table 2 The values of k_{inh} at different [formic acid] at pH = 7.34, t = 33 ^{o}C Na$_2$HPO$_4$ =8x10^{-2} mol L^{-1}, KH$_2$PO$_4$ = 2x10^{-2} mol L^{-1}.

[formic acid] mol dm^{-3}	$10^3 k_{F.A}$ s^{-1}	$1/k_{F.A}$ s
3.0x10^{-5}	0.23	4347
6.0x10^{-5}	0.21	4761
8.0x10^{-5}	0.20	5000
1.0x10^{-4}	0.19	5263
3.0x10^{-4}	0.18	5555
6.0x10^{-4}	0.14	7142
8.0x10^{-4}	0.12	8333

The valuve of first order rate constant k_{inh} in the presence of formic acid decreased with increasing [formic acid] in agreement with the rate law.

$$k_{inh} = k_1/(1+B\,[F.A.]\,) \tag{4}$$

Where B is inhibition parameter for rate inhibition by organics

The equation (4) on rearrangement becomes

$$1/\,k_{inh} = 1/\,k_1+ B\,[F.A.]\,/\,k_1 \tag{5}$$

In accordance with the equation (5) the plot of $1/\,k_{inh.}$ v/s [formic acid] was found to be linear with positive intercept. The values of intercept $(1/\,k_1)$ and slope $(B/\,k_1)$ were found to be 4.4x10^3 mol dm^{-3}s and 4.6x10^6 at pH = 7.34, t = 33°C From these values the value of inhibition parameter B was found to be 1.0x10^3 mol dm^{-3}
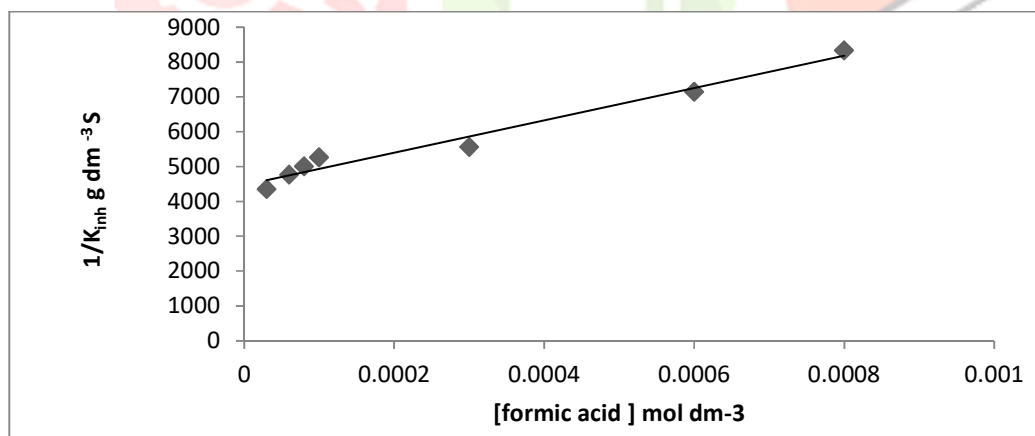

Fig.2 -Effect of formic acid at [S(IV)]=3x10^{-3} mol dm-3 pH=7.34 and temp=33°C in alkaline buffered medium.

CoO Catalysed Reaction

The kinetics of CoO Catalysed autoxidation of S(IV) was studied in alkaline medium in the absence of inhibitor formic acid

[S(IV)] Variation

The dependence of S(IV) on reaction rate was studied by varying [S(IV)] from 1×10^{-3} mol dm^{-3} to 5×10^{-3} moldm^{-3} at two different but fixed [CoO] of 0.01 and 0.02 g dm^{-3} at pH = 7.34, t = 33 ^{o} The kinetics was found to be first order in [S(IV)] v/s time 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)=3×10^{-3} mol dm^{-3} pH=7.34, t= 33°C in alkaline buffer medium. The values of first order rate constant k_{cat} for S(IV) oxidation was determine are shown in fig 3. The nature of dependence of k_{cat} on CoO was indicated as two term rate law (6)

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

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

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 1.7×10^{-3} mol dm^{-3} s at pH = 7.34, t = 33°C, in alkaline buffered medium.
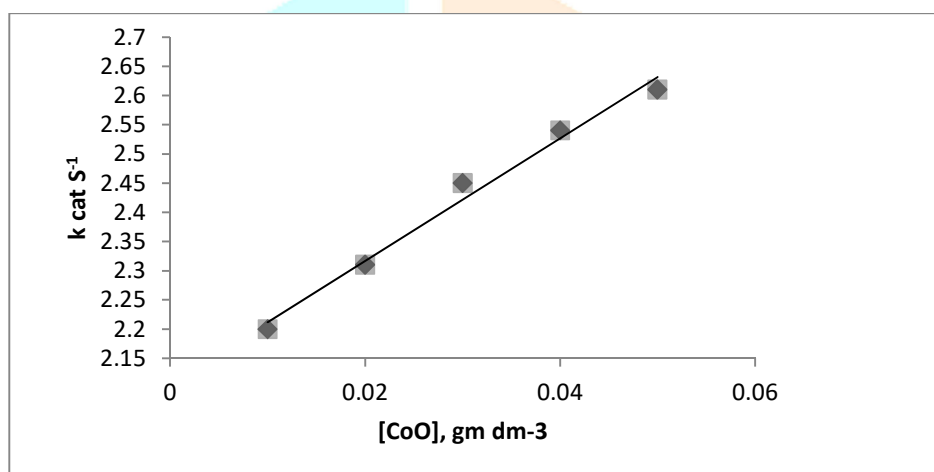
Fig.3- The dependence of catalyst concentration at [S(IV)] = 3×10^{-3} mol dm^{-3} pH = 7.34, t = 33 ^{o}C, in alkaline buffered medium.

Variation of pH

The investigation involved a systematic exploration of pH variation within the range of 7.34 to 9.40, different concentrations of S(IV), CoO, and Formic acid, temperatures. The rate decreases slightly by varying pH is inverse H$^+$ ion dependence was observed. From the plot of log k_1 v/s log (H$^+$). The effect of [buffer] was examined by varying the concentration of both Na$_2$HPO$_4$ & KH$_2$PO$_4$ so that the ratio [Na$_2$HPO$_4$]/[KH$_2$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-3 Effect of $_p$H at [S(IV)] = 3×10^{-3} mol dm^{-3} at CoO = 0.02gm dm^{-3}, [formic acid]= 6×10^{-4} mol dm^{-3}, Na$_2$HPO$_4$ = 8×10^{-2} molL^{-1} KH$_2$PO$_4$ = 2×10^{-2} mol L^{-1}.

$_p$H	7.34	8.55	8.96	9.40
$10^3 k_{F.A}$ s^{-1}	0.95	1.19	1.26	1.32

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 formic acid revealed that the kinetics remain first order both in S(IV) and [CoO] and independence of pH obeys the following rate law.

$$-d[S(IV)]/dt = (k_1 + k_2[CoO][S(IV)])/1 + B\ (F.A.) \qquad (8)$$

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

$$1/k_{inh} = 1 + B\ (F.A.)/k_{cat} \qquad (10)$$

$$1/k_{inh} = 1/k_{cat} + B\ (F.A)/k_{cat} \qquad (11)$$

Table- 4 The values of k_{inh} at different [formic acid] at [S(IV)]=$3x10^{-3}$mol dm^{-3} ·CoO=0.02gm dm^{-3} , pH = 7.34, t = 33 ^{o}C Na$_2$HPO$_4$ = $8x10^{-2}$ molL^{-1} KH$_2$PO$_4$ = $2x10^{-2}$ mol L^{-1}.

[formic acid] mol dm^{-3}	$10^3 k_{F.A}$ s^{-1}	$1/k_{F.A}$ s
$3.0x10^{-5}$	1.90	526
$6.0x10^{-5}$	1.91	523
$8.0x10^{-5}$	1.70	588
$1.0x10^{-4}$	1.90	526
$3.0x10^{-4}$	1.38	724
$6.0x10^{-4}$	0.95	1052
$8.0x10^{-4}$	0.80	1250
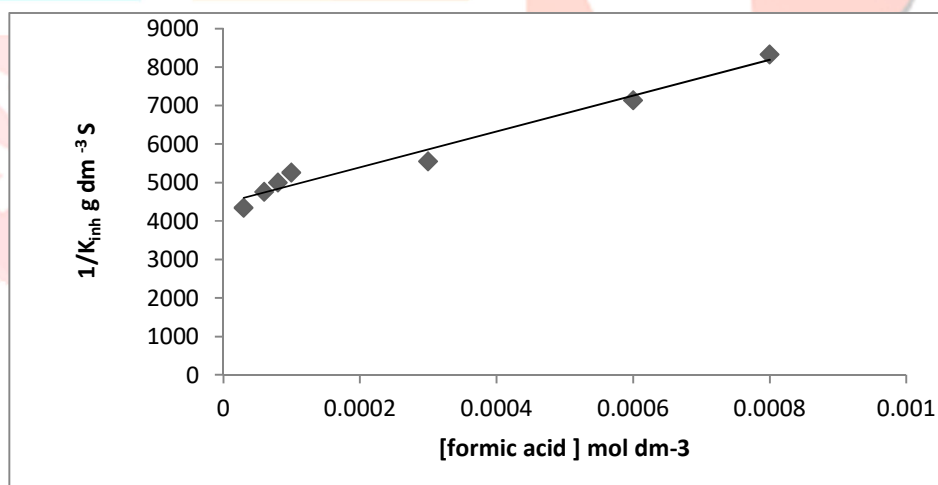
Fig.4- Effect of formic acid at [S(IV)]=$3x10^{-3}$ mol dm^{-3} , [CoO]=0.02gm dm^{-3} , pH=7.34 and temp=33°C in alkaline buffered medium.

By plotting a graph between $1/k_{inh}$ versus [formic acid] 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 4.7×10^2 s and 9.6×10^5 mol^{-1} dm^3 s separately. From these values the value of inhibition parameter B can be determined, inhibition parameter B = slope/Intercept that is B = 2.0×10^3 mol^{-1} dm^3.
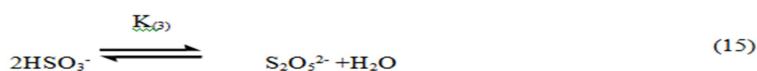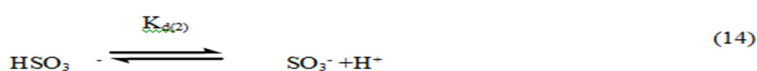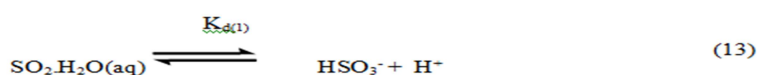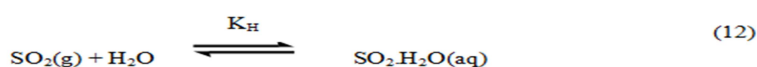
Effect of temperature-The values of k_{obs} were determined at different temperatures in the range of 33°C to 48°C. The results are given in Table 5. By plotting a graph between log k v/s 1/t yield us an apparent empirical energy of activation 31.21 kJ mol^{-1} in the presence of formic acid.

Table 5 Effect of temperature at [S(IV)] = 3×10^{-3} mol dm^{-3} at CoO= 0.02 g dm^{-3} [formic acid]= 6×10^{-4} mol dm^{-3} pH =7.34 Na$_2$HPO$_4$ = 8×10^{-2} molL^{-1} KH$_2$PO$_4$ = 2×10^{-2} mol L^{-1}.

t °C	33°C	38 °C	43 °C	48°C
$10^3 k_{F.A}$ S^{-1}	0.95	1.24	1.41	1.72

DISCUSSION-

In aqueous solution SO$_2$ is present in four forms SO$_2$.H$_2$O, HSO$_3^{-1}$, SO$_3^{-2}$, S$_2$O$_3^{-2}$ governed by the following equations.

$$SO_2(g) + H_2O \xrightleftharpoons{K_H} SO_2.H_2O(aq) \qquad (12)$$

$$SO_2.H_2O(aq) \xrightleftharpoons{K_{d(1)}} HSO_3^- + H^+ \qquad (13)$$

$$HSO_3^- \xrightleftharpoons{K_{d(2)}} SO_3^- + H^+ \qquad (14)$$

$$2HSO_3^- \xrightleftharpoons{K_{(3)}} S_2O_5^{2-} + H_2O \qquad (15)$$

K_H is Henry"s constant and K_1, K_2 are acid dissociation constants. K_3 is the consistent arrangement for $S_2O_5^{2-}$ at 25°C the qualities are $K_H = 1.23$ mol L^{-1}atm^{-1}, $K_1 = 1.4 \times 10^{-2}$, $K_2 = 6.24 \times 10^{-8}$, also $K_3 = 7.6 \times 10^{-2}$. In this test concentrated in the pH range (7.34- 9.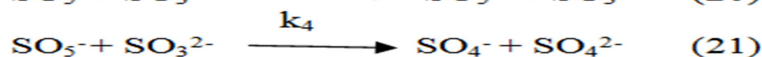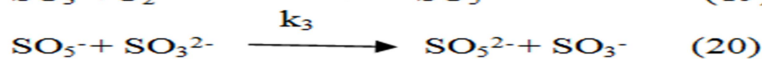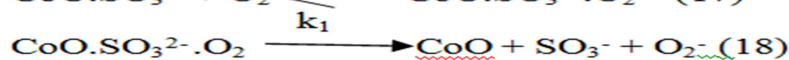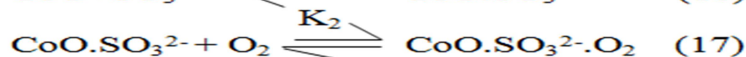40), S(IV) would generally be present as SO_3^{2-}. Since the reaction rate of under study not dependent on pH, we have considered that only SO_3^2 species to be reactive. In some modifications the autoxidation reactions of sulfur (IV) take place in the heterogeneous aqueous phase catalysed by a metallic 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[18] 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)[19] studied the influence of alcohols such as methanol, ethanol, propanol and butanol on the reaction between sodium sulfite and O$_2$ and found that these alcohols limited the reaction rate. Backstrom (1929)[20] 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)[8] proposed a mechanism to prevent a highly inhibitory oxidation reaction in the chain between sodium sulfite and oxygen. Connick and Zhang (1996)[21] reported that when Mn^{+2} particles are considered, methanol inhibition is more unpredictable. Grgic et al. (1998)[22] 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 (2006)[23] et al. investigated the influence of carboxylic acids on the Mn (II) catalyzed oxidation of sulfur (IV) and found that monocarboxylic 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.[24]. This shows the activity of a radical mechanism that includes oxysulfur -free radicals, such as $SO_3- \bullet$, $SO_4- \bullet$ and $SO_5- \bullet$ [24,25,26]. The inhibition is caused by the interception of $SO_4- \bullet$ by inhibitors such as ethanol and benzene, etc. Gupta et al.[24] a radical mechanism operate has been reported to work on reaction where the value of inhibition parameter is between 10^3 and 10^4. In the current study, the inhibition parameter is found to be 1.0×10^3 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[27-29]

$$CoO + SO_3{}^{2-} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} CoO.SO_3{}^{2-} \qquad (16)$$

$$CoO.SO_3{}^{2-} + O_2 \overset{K_2}{\rightleftharpoons} CoO.SO_3{}^{2-}.O_2 \qquad (17)$$

$$CoO.SO_3{}^{2-}.O_2 \overset{k_1}{\longrightarrow} CoO + SO_3{}^- + O_2{}^- \qquad (18)$$

$$SO_3{}^- + O_2 \overset{k_2}{\longrightarrow} SO_5{}^- \qquad (19)$$

$$SO_5{}^- + SO_3{}^{2-} \overset{k_3}{\longrightarrow} SO_5{}^{2-} + SO_3{}^- \qquad (20)$$

$$SO_5{}^- + SO_3{}^{2-} \overset{k_4}{\longrightarrow} SO_4{}^- + SO_4{}^{2-} \qquad (21)$$

$$SO_5{}^{2-} + SO_3{}^{2-} \overset{k_5}{\longrightarrow} 2SO_4{}^{2-} \qquad (22)$$

$$SO_4{}^- + SO_3{}^{2-} \overset{k_6}{\longrightarrow} SO_4{}^{2-} + SO_3{}^- \qquad (23)$$

$$SO_4{}^- + x \overset{k_7}{\longrightarrow} \text{Non chain product} \qquad (24)$$

$$SO_4{}^- + \text{Formic acid} \overset{k_8}{\longrightarrow} \text{Nonchain product} \qquad (25)$$
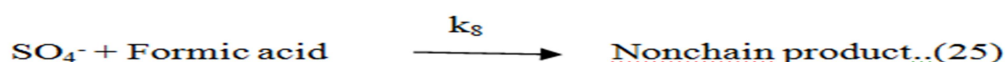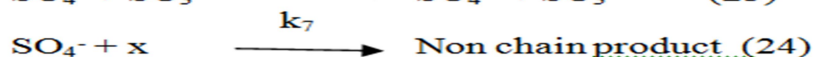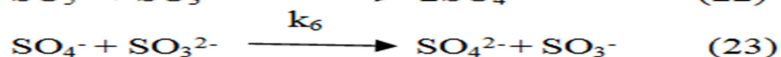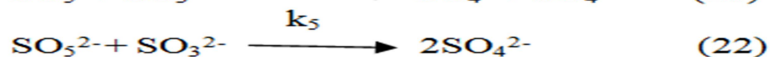
In the mechanism, no role is assigned to $O_2{}^-$, which is also known to react with sulfur (IV) slowly. It may disproportionate to form H_2O_2 and O_2 or may be scavenged by impurities. By assuming long chain hypothesis and steady state approximation $d[SO_3{}^-]/dt$, $d[SO_4{}^-]/dt$ and $d[SO_5{}^-]/dt$ to zero it can be shown that the rate of initiation is equal to the rate of termination. (Eq. 26)

$$k_1[CoO(SO_3{}^{2-})(O_2)] = \{k_7[X] + k_8[\text{formic acid}]\}[SO_4{}^{-\bullet}] \qquad (26)$$

Since the reaction is completely stopped in the presence of formic acid at 8×10^{-4} mol dm^{-3}, So the steps (18) and (22) appear to be unimportant. The contribution of propagation reaction (Eq. 21) been significant in the CoO catalysed. Reaction where the autoxidation reaction should have occurred even in the presence of high formic acid concentration i.e. the reaction is completed seized in the presence of high concentration of formic acid. This led us to ignore the step (Eq.21) and assume only the rate of reaction given by equation- (27).

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

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

$$R_{cat} = \frac{k_6 k_1 [CoO.SO_3{}^{2-}.O_2][SO_3{}^{2-}]}{k_7[x] + k_8[F.A.]} \qquad (28)$$

From equilibrium Eq. 16 and Eq. 17

$$R_{cat} = \frac{k_6 K_1 K_2 [CoO][S(IV)][O_2]}{\{1 + k_1[S(IV)]k_7[x] + k_8[F.A.]\}} \qquad (29)$$

At fixed O_2, replacing $k_6 K_1 K_2 [O_2]$ by k^1 we get

$$R_{cat} = \frac{k^1 [CoO][S(IV)]}{\{1+k_1[S(IV)]k_7[x] +k_8 [F.A.]\}} \qquad (30)$$

Since we observe a first order in [S(IV)], The value of $k_1[S(IV)] \ll 1$ so the above rate law can be reduce to

$$R_{cat} = \frac{k^1 [CoO][S(IV)]}{k_7[x] +k_8 [F.A.]} \qquad (31)$$

Gupta et al.[24] 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 $2.0 \times 10^3 mol^{-1}dm^3$. Which is in the range of 10^3 to 10^5. So on the basis of calculated value of B, we concluded that formic acid 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 system.

CONCLUSION

The conclusions are deduced from the results of the formic acid inhibited CoO catalysed autoxidation of S(IV) was that inhibit the oxidation 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 operatives.

FUTURE SCOPE

The results are useful for modeling rain water acidity and therefore a great use of meteorology and impressive chemistry. This study is important in understanding the mechanism of the atmospheric oxidation of S(IV) by O_2.

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