

## Mechanistic Study of Reaction between 5-Sulfosalicylic Acid and Colloidal MnO<sub>2</sub>

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The reaction between 5-sulfosalicylic acid (5-SSA) and colloidal MnO<sub>2</sub> has been studied kinetically in acidic medium. During the reaction the concentration of 5-SSA was kept highly excess than the concentration of colloidal MnO<sub>2</sub> to maintain the pseudo-first-order condition. The reaction was studied by following decrease in absorbance of colloidal MnO<sub>2</sub> at 390 nm and the first order rate constants were determined from linear log (Abs.) against time plots. The linearity of the first-order plots did not involve any autocatalytic part. The oxidation of 5-sulfosalicylic acid (5-SSA) by colloidal MnO<sub>2</sub> involves intervention of free radicals and Mn(III). The product of reaction in colloidal MnO<sub>2</sub> was *p*-hydroxy benzene sulfonate ion as confirmed by LCMS-MS analysis. The oxidation by colloidal MnO<sub>2</sub> consists of acid dependent and independent mechanisms. The results of added Mn(II), Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and acrylonitrile indicate involvement of Mn(III) and free radical during oxidation by colloidal MnO<sub>2</sub>. The probable mechanisms for acid dependent and independent paths were predicted and the rate expressions were also obtained. The activation parameters also support the proposed mechanisms.

**Keywords:** Kinetic studies, Oxidation, 5-Sulfosalicylic acid, Colloidal MnO<sub>2</sub>.

### INTRODUCTION

5-Sulfosalicylic acid (5-SSA) having both carboxylic acid and sulfonic acid group along with phenolic-OH has potential applications in various fields. In the field of analytical chemistry, 5-sulfosalicylic acid (5-SSA) finds various applications, including protein determination, sugar detection, as redox indicator and chelating agent [1-4]. It has also been used as an organo-catalyst for various organic transformations [5-9]. Highly stable 5-SSA is becoming an environmental threat, due to its excessive industrial use [10-12], as it has been used as pharmaceutical personal care product (PPCP). As a result of high stability of 5-SSA towards less efficient biological degradation methods several advanced oxidation processes (AOPs) have been developed [12] for its removal from wastewaters. The AOPs involve oxidative [13], photocatalytic [12,14], electrochemical [15] and ozonization [16]. Apart from the above significances of 5-SSA, it posses a phenolic OH and after oxidation a quinone will be generated and such quinones are now investigated for their utilization in all aqueous redox flow batteries [16]. Presence of sulfonic acid group makes them good applicants for such uses due to the fact that quinones sulfonates have higher solub-

ility in water [17,18]. Therefore, redox chemistry of sulfonic acid derivatives of hydroxy benzoic acids has received considerable attention in recent past [10-12,17,18].

The 5-SSA has a good chelating agent [19-22], which forms stable complexes with metal ions like Fe<sup>3+</sup>. Such complexes are utilized for developing an alternative method for chemical oxygen demand [19] and for effective cancer therapy [20]. Due to formation of stable complexes the oxidation of 5-SSA have not been investigated by metal ions, which are also strong oxidizing agents. Therefore, oxidation of 5-SSA can be studied by reagents like ditelluratocuprate(III) ions, where the metal ion is already in the complex form [23] proceeds through a weak precursor complex formation. The study of interaction of 5-SSA with a metal ion immune to formation of stable complex would be quite interesting. Colloidal MnO<sub>2</sub> is also an oxidant suspended in solution thus formation of the stable complex with substrates like 5-SSA is difficult. Since manganese in the +4 state has strong oxidizing properties, colloidal MnO<sub>2</sub> was utilized as an oxidant for 5-SSA in the present study. The possibility of formation of stable complex by 5-SSA is with an oxidant in colloidal state is less possible, which enable to study the oxidation pathway without any complex mechanism.

Therefore, the reaction between 5-SSA and colloidal  $\text{MnO}_2$  is investigated to understand the probable pathway of the oxidation of 5-SSA.

## EXPERIMENTAL

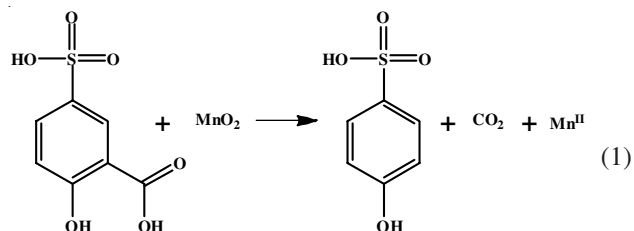
5-Sulfosalicylic acid (5-SSA) was purchased from TCI, India and its solutions were freshly prepared in double-distilled water. Perchloric acid (Loba A.R.) was diluted to obtain required concentrations of stock solution in double-distilled water. To maintain the ionic strength sodium perchlorate was utilized which was obtained by mixing equivalent volumes of perchloric acid and sodium hydroxide solution.

**Synthesis and colloidal  $\text{MnO}_2$ :** Colloidal  $\text{MnO}_2$  was synthesized by adding  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{KMnO}_4$  slowly to  $1.87 \times 10^{-4} \text{ mol dm}^{-3}$  solution of sodium thiosulphate and then diluted the mixture to the required volume [24-26].

**Kinetic measurements:** In order to measure the decreasing concentration of colloidal  $\text{MnO}_2$  over time, the absorbance at 390 nm was measured using a Systronics VISIBLE-SPECTRO 105 spectrophotometer. The [5-SSA] was always more than ten times than that of [oxidant] at 30 °C. To initiate the reaction the required volumes of solutions of 5-SSA, colloidal  $\text{MnO}_2$ , perchloric acid and sodium perchlorate at constant temperature were mixed. The advancement of reaction was pursued spectrophotometrically at 390 nm for colloidal  $\text{MnO}_2$ . The rate constants were calculated from the  $\log[\text{Abs}]$  against time plots.

## RESULTS AND DISCUSSION

**Reaction stoichiometry:** For the determination of stoichiometry of the reaction concentration of colloidal  $\text{MnO}_2$  mixtures containing  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and that of 5-SSA ( $1.0 \times 10^{-4}$  to  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) were prepared. The remaining concentration of colloidal  $\text{MnO}_2$  was determined up to a week after each 24 h spectrophotometrically till the absorbance value is constant. Each mole of colloidal  $\text{MnO}_2$  was consumed per mole of 5-SSA. Further, a solution containing  $4.0 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{MnO}_2$  and  $1.3 \times 10^{-2} \text{ mol dm}^{-3}$  of 5-SSA was kept undisturbed up to 72 h. The resulting solution was neutralized with NaOH and filtered. The filtrate was analyzed with Bruker IMPACT HD LCMS-MS instrument. The spectrum shows peak at 175  $m/z$  corresponding to 4-hydroxy benzene sulfonic acid (Fig. 1). Therefore, from the spectrophotometric analysis and LCMS-MS analysis the stoichiometry of the reaction can be given as eqn. 1.



**Effect of [oxidant], [5-SSA] and  $[\text{H}^+]$ :** To understand the effect of colloidal  $\text{MnO}_2$  and 5-SSA, the  $[\text{HClO}_4]$  ( $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) and at ionic strength ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) at 30 °C were unchanged and the kinetic data were obtained by chan-

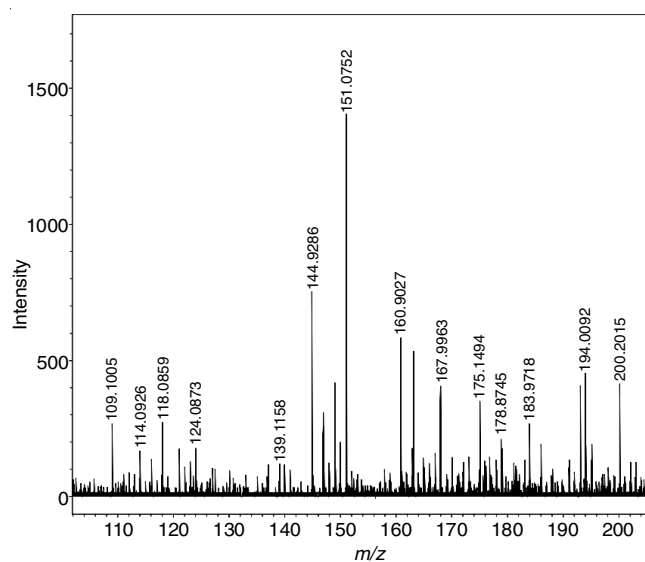


Fig. 1. LCMSMS spectrum of reaction mixture of oxidation of 5-SSA by colloidal  $\text{MnO}_2$

ging either [5-SSA] ( $0.1 \times 10^{-3}$  to  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) at  $[\text{MnO}_2]$  ( $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) or  $[\text{MnO}_2]$  ( $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) at [5-sulfosalicylic acid] ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) (Table-1). The values of rate constants,  $k_{\text{obs}}$ , were found to depend on the [5-SSA] (Table-1) and the plot of  $(1/k_{\text{obs}})$  against  $(1/[5\text{-SSA}])$  was also found to be a straight line passing through origin. As mentioned earlier the plots of  $\log(\text{Abs})$  4% time did not contain any autocatalytic part showing unit order dependence of the reaction in  $[\text{MnO}_2]$ . The values of  $k_{\text{obs}}$  remain constant as  $[\text{MnO}_2]$  changes, which also support order in [oxidant] is one (Table-1).

$10^5 [\text{MnO}_2]$ ( $\text{mol dm}^{-3}$ )	$10^3 [5\text{-SSA}]$ ( $\text{mol dm}^{-3}$ )	$10^5 k_{\text{obs}}$ ( $\text{s}^{-1}$ )
1.0	1.0	11.2
2.0	1.0	11.3
3.0	1.0	11.9
4.0	1.0	11.2
5.0	1.0	11.7
6.0	1.0	11.8
8.0	1.0	11.9
10.0	1.0	11.3
1.0	1.0	11.3
1.0	2.0	16.5
1.0	3.0	19.6
1.0	4.0	23.5
1.0	5.0	27.6
1.0	6.0	28.3
1.0	8.0	31.2
1.0	10.0	34.5

To obtain the information of any involvement of hydrogen ions in prior equilibria either with colloidal  $\text{MnO}_2$  or with 5-SSA, the  $[\text{HClO}_4]$  was changed from 0 to  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and values of  $k_{\text{obs}}$  were determined. Acceleration of rate of reaction is observed by  $\text{HClO}_4$  (Table-2) and the plot of

TABLE-2 RESULTS OF VARIATION OF [HClO <sub>4</sub> ] AND THE k <sub>obs</sub> VALUES OF REACTION BETWEEN 5-SULFOSALICYLIC ACID (5-SSA) BY COLLOIDAL MnO <sub>2</sub> AT 30 °C 10 <sup>3</sup> [5-SSA] = 1.0 mol dm <sup>-3</sup> , 10 <sup>5</sup> [MnO <sub>2</sub> ] = 1.0 mol dm <sup>-3</sup> and I = 1.0 × 10 <sup>-3</sup> mol dm <sup>-3</sup>			
10 <sup>4</sup> [HClO <sub>4</sub> ] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )	10 <sup>4</sup> [HClO <sub>4</sub> ] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )
0.0	7.27	5.0	15.7
1.0	9.19	6.0	18.6
2.0	11.4	8.0	21.3
3.0	12.5	10.0	25.0

k<sub>obs</sub> against [HClO<sub>4</sub>] was found to be a straight line with a positive intercept (Fig. 2).

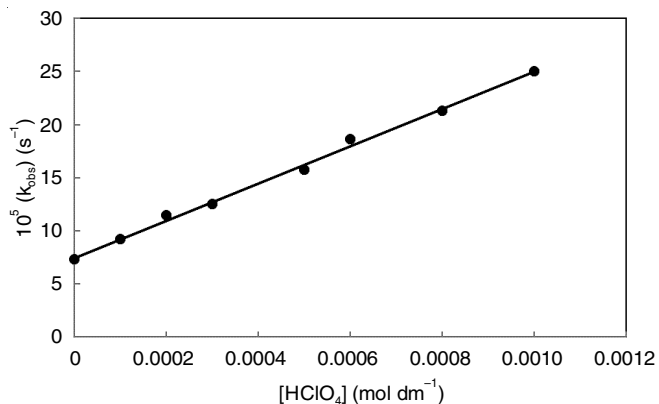


Fig. 2. Plot k<sub>obs</sub> against [HClO<sub>4</sub>] for oxidation of 5-SSA by colloidal MnO<sub>2</sub> (conditions as in Table-2)

#### Effect of added tetrasodium pyrophosphate Mn(II):

Since, colloidal MnO<sub>2</sub> is known to be reduced to Mn(II) ions when it reacts with a substrate. The path of the reaction may be of direct two electron or two single electron transfer steps. During the two electron transfer steps, no free radical or Mn(III) is expected while in case of two single electron transfer steps such intervention is possible. To check whether free radical is formed reaction a free radical scavenger acrylonitrile was added to the solution containing colloidal MnO<sub>2</sub> and 5-SSA. Appearance of precipitate as a result of polymerization acrylonitrile approves formation of polyacrylonitrile. Further, intervention of Mn(III) was also examined by adding excess of tetrasodium pyrophosphate (Table-3) and Mn(II). The k<sub>obs</sub> values increased by the addition of tetrasodium pyrophosphate and

TABLE-3 RESULTS OF VARIATION OF [Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ] AND [Mn(II)] AND THE CORRESPONDING k <sub>obs</sub> VALUES OF OXIDATION OF 5-SULFOSALICYLIC ACID (5-SSA) BY COLLOIDAL MnO <sub>2</sub> AT 30 °C 10 <sup>5</sup> [MnO <sub>2</sub> ] = 1.0 mol dm <sup>-3</sup> , 10 <sup>3</sup> [5-SSA] = 1.0 mol dm <sup>-3</sup> , 10 <sup>4</sup> [HClO <sub>4</sub> ] = 2.0 mol dm <sup>-3</sup> and I = 1.0 × 10 <sup>-3</sup> mol dm <sup>-3</sup>			
10 <sup>3</sup> [Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )	10 <sup>3</sup> [Mn(II)] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )
1.0	12.2	1.0	13.5
2.0	13.8	2.0	19.8
4.0	15.4	4.0	31.4
6.0	17.3	6.0	47.5
8.0	21.1	8.0	51.3
10.0	23.7	10.0	68.2

Mn(II) indicating intervention of Mn(III) in the reaction which also support the formation of polyacrylonitrile during the course of the reaction.

**Effect of temperature:** The result of increase in temperature from 10, 20, 25, 30 and 40 °C led to the calculation of activation parameters and are given in Table-4.

TABLE-4 RESULTS OF VARIATION OF TEMPERATURE AND THE CORRESPONDING k <sub>obs</sub> VALUES OF REACTION BETWEEN 5-SSA AND COLLOIDAL MnO <sub>2</sub> AND ACTIVATION PARAMETERS 10 <sup>5</sup> [MnO <sub>2</sub> ] = 1.0 mol dm <sup>-3</sup> , 10 <sup>3</sup> [5-SSA] = 1.0 mol dm <sup>-3</sup> , 10 <sup>4</sup> [HClO <sub>4</sub> ] = 2.0 mol dm <sup>-3</sup> and I = 1.0 × 10 <sup>-3</sup> mol dm <sup>-3</sup>	
T (K)	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )
283	6.14
293	7.77
298	9.98
303	11.2
313	14.2
E <sub>a</sub> (kJ mol <sup>-1</sup> )	21.2
ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	18.8
ΔG <sup>‡</sup> (kJ mol <sup>-1</sup> )	47.1
-ΔS <sup>‡</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	94.9

Since, the results of variation of colloidal MnO<sub>2</sub> and 5-SSA (Table-1) show overall second order reaction unit each both the reactants. Since the oxidant is in the colloidal form the reaction is initiated by the adsorption of the 5-SSA on the superficial layer of the oxidant [27-30]. The first order dependance of the reaction on [MnO<sub>2</sub>] is verified by the linearity of the log Abs against time plots. The k<sub>obs</sub> values increase as the [5-SSA] and [HClO<sub>4</sub>] increase (Table-1). From Fig. 2, it can also be observed that the reaction also occurs in absence of HClO<sub>4</sub> also. The pK<sub>a</sub> sulfonic acid group of 5-SSA [31] is -2.8 therefore, it exists completely in the dissociated form under the reaction conditions, while the pK<sub>a</sub> of carboxylic acid [32] is 2.97 which exists both in the unprotonated and the protonated form. The calculated concentration of unprotonated, the carboxylate anion, increases non-linearly while that of the protonated form decreases with increase in [HClO<sub>4</sub>]. The acceleration of k<sub>obs</sub> values (Scheme-I) by the [HClO<sub>4</sub>] thus confirms the protonated 5-SSA as the active species of the substrate. Such an accelerating effect

$$\text{Rate} = k_1[C_1] + k_2[C_2] \quad (2)$$

$$\text{Rate} = k_1K_1[\text{RCOOH}][\text{MnO}_2] + k_2K_1K_2[\text{H}^+][\text{RCOOH}][\text{MnO}_2] \quad (3)$$

$$[\text{MnO}_2]_T = [\text{MnO}_2]_f + [C_1] + [C_2] \quad (4)$$

$$[\text{MnO}_2]_T = [\text{MnO}_2]_f + K_1[\text{RCOOH}][\text{MnO}_2]_f + K_1K_2[\text{H}^+][\text{RCOOH}][\text{MnO}_2]_f$$

$$[\text{MnO}_2]_T = [\text{MnO}_2]_f (1 + K_1[\text{RCOOH}] + K_1K_2[\text{H}^+][\text{RCOOH}])$$

$$[\text{MnO}_2]_T = [\text{MnO}_2]_f (1 + K_1 + K_1K_2[\text{H}^+][\text{RCOOH}])$$

$$[\text{MnO}_2]_f = [\text{MnO}_2]_T / (1 + K_1 + K_1K_2[\text{H}^+][\text{RCOOH}]) \quad (5)$$

$$\text{Rate} = (k_1K_1 + k_2K_1K_2[\text{H}^+][\text{RCOOH}])[\text{MnO}_2]$$

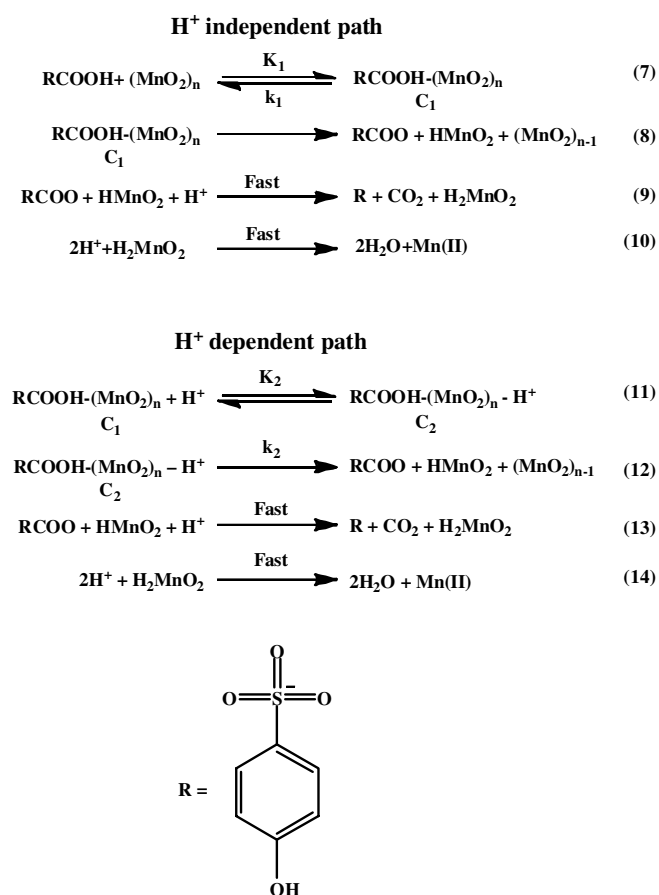
$$\text{Rate} = \frac{(k_1K_1 + k_2K_1K_2[\text{H}^+][\text{RCOOH}])[\text{MnO}_2]}{(1 + K_1 + K_1K_2[\text{H}^+][\text{RCOOH}])}$$

$$\text{Rate}/[\text{MnO}_2] = k_{\text{obs}} = \frac{(k_1K_1 + k_2K_1K_2[\text{H}^+][\text{RCOOH}])}{(1 + K_1 + K_1K_2[\text{H}^+][\text{RCOOH}])} \quad (6)$$

Scheme-I

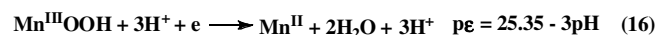
of  $[\text{HClO}_4]$  can be explained due to direct involvement [27-30] of the  $[\text{H}^+]$  ion in the slow step of the reaction. The intervention of free radicals as tested with acrylonitrile, the increase in the rate of reaction in presence of added Mn(II) and  $\text{P}_2\text{O}_7^-$  indicate the development of Mn(III) as an intermediate [27-30] in the reaction.

The mechanism of oxidation of 5-sulfosalicylic acid by colloidal  $\text{MnO}_2$  can be represented as in **Scheme-II** based on the results obtained. According to **Scheme-II**, the oxidation of 5-sulfosalicylic acid involves an acid independent and dependent path. Initially, 5-SSA is absorbed on the superficial layer of colloidal  $\text{MnO}_2$  units with an equilibrium constant  $K_1$  forming and absorbed complex  $C_1$ , eqn. 7 of **Scheme-II** in both paths. The complex  $C_1$  decays in a slow step in acid independent path as in eqn. 8 with rate constant  $k_1$ . In the acid dependent path of **Scheme-II**, the complex  $C_1$  undergo protonation forming another complex  $C_2$  with an equilibrium constant  $K_2$  as shown in eqn. 11. The second complex,  $C_2$ , also decomposes in a slow step with rate constant  $k_2$  as in eqn. 12. Both complexes  $C_1$  and  $C_2$  undergo one electron transfer to generate carboxylate free radical and  $\text{HMnO}_2$ . Formation of  $\text{HMnO}_2$  (Mn<sup>III</sup>) and carboxylate free radical has been verified experimentally by studying the effect of Mn<sup>II</sup>, tetrasodium pyrophosphate and acrylonitrile on the reaction (Table-3). The final product of the reaction was found to be *p*-hydroxybenzene sulfonate anion as observed in the LCMS analysis (Fig. 1).



**Scheme-I:** Mechanism of oxidation of 5-sulfosalicylic acid by colloidal  $\text{MnO}_2$

The oxidation-reduction potential of  $\text{MnO}_2$  depends on pH of the solution. The values for  $\text{MnO}_2/\text{HMnO}_2$  and  $\text{HMnO}_2/\text{Mn}^{\text{II}}$  couples [33] at pH = 3.69 of the present reaction conditions can be calculated by as 0.74 V and 0.84 V, respectively. The redox potentials were calculated by using the following formulae as in eqns. 10 and 11. It has also been observed that the oxidation of phenol is second order at pH 1-2 and requires higher temperature [34] at higher pH while in alkaline medium oxidation [35] of phenol does not occur. It is also reported that the desulfonation of benzenesulfonic acids requires higher temperatures [36]. Therefore, under the present conditions further oxidation of *o*-hydroxy benzene sulfonate ion does not occur and remains unaffected and is the final product of the reaction.



The rate for both  $[\text{H}^+]$  ion independent and dependent paths of the reaction can be obtained as follows. Considering both the acid independent and dependent paths as they occur simultaneously the rate of the reaction is given as in eqn. 2. Substituting for  $[C_1]$  and  $[C_2]$  from equilibriums (eqns. 7 and 11) of **Scheme-I**, we get eqn. 3. But the oxidant exists in both  $C_1$  and  $C_2$  and as free  $[\text{MnO}_2]_f$  which after substituting for  $[C_1]$  and  $[C_2]$  and simplifying  $[\text{MnO}_2]_f$  can be obtained as in eqn. 5. The final expression for the rate of the reaction can be obtained by combining eqns. 2 and 5. The expression for  $k_{\text{obs}}$  will then be as given in eqn. 6. According to eqn. 6, plot of  $k_{\text{obs}}$  against  $[\text{H}^+]$  will be a straight line with an intercept (Fig. 2). The activation energy is very low indicating that only decarboxylation of 5-SSA is possible. Further oxidation to either desulfonation or quinone formation would have resulted in higher activation energy as both reactions required harsh conditions [34-36]. Moderate change in enthalpy of activation and the free energy of oxidation also indicate the ease of oxidation of 5-SSA. Low activation entropy also indicate surface adsorption of 5-SSA on the surface of  $\text{MnO}_2$ .

## Conclusion

The oxidation of 5-sulfosalicylic acid (5-SSA) by colloidal  $\text{MnO}_2$  has been investigated kinetically. The product of oxidation is *p*-hydroxy benzene sulfonate ion. The oxidation by colloidal  $\text{MnO}_2$  was studied in  $2.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of  $\text{HClO}_4$ . A mechanism of oxidation by colloidal  $\text{MnO}_2$  was proposed involving formation of Mn(III) and free radical. The formation of Mn(III) and free radicals during oxidation of colloidal  $\text{MnO}_2$  is supported by effect of acrylonitrile. The mechanism of oxidation by colloidal  $\text{MnO}_2$  involves both acid independent and dependent paths. The activation parameters were also determined by the effect of temperature on the values of  $k_{\text{obs}}$  and support the proposed mechanisms.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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