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Waugh Type Polyoxometalate Enneamolybdomangate(IV) as an Acid Catalyst for Hydrolysis and as an Oxidant for Aspirin: A Kinetic Study

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The oxidation of aspirin and salicylic acid by enneamolybdomanganate(IV) were studied in perchloric acid medium. The aspirin undergo hydrolysis prior to the oxidation to generate salicylic acid, which was found to be catalyzed by both $HClO_4$ as well as the oxidant. The rate of hydrolysis of aspirin catalyzed by the oxidant was found to be lesser than that of $HClO_4$. A mechanism based on the kinetic results is proposed for oxidation of both aspirin and salicylic acid. Initially, aspirin undergo hydrolysis to give salicylic acid, which is catalyzed by both the oxidant, which also acts as an acid catalyst and the $HClO_4$ used. The salicylic acid generated in prior hydrolysis reacts with an oxidant undergoing oxidative decarboxylation by enneamolybdomanganate(IV) in a rate determining step generating phenol. Further oxidation of phenol by another oxidant molecule gives the final product *p*-benzoquinone in a fast step. The mechanism of oxidation of salicylic acid was also studied under identical conditions as that of aspirin and found to be similar except its prior hydrolysis. A plausible mechanism was proposed and the rate laws for both the substrates were derived. In order to understand the intervention of free radicals the reaction was studied in presence of added acrylonitrile. The formation of copious precipitate due to polymerization of added acrylonitrile was not observed and the values of k_{obs} also remain constant in presence of added acrylonitrile. The formation of Mn^{III} was also studied in presence of added tetrasodium pyrophosphate, which did not affect the values of k_{obs}. Therefore, the formation of free radical and Mn^{III} was excluded while proposing mechanisms for both the substrates. The effect of added products Mn^{2+} and molybdate also did not have any effects indicating no prior equilibria involving these two products. The effect of ionic strength and solvent polarity are in favour of the reaction between two neutral molecules. The activation parameters were determined and support an outer sphere reaction with formation of a weak precursor complex between the reactants was proposed for both aspirin and salicylic acid.

Keywords: Waugh type polyoxometalate, Enneamolybdomangate(IV), Acid catalyst, Hydrolysis, Oxidant, Aspirin, Salicylic acid.

INTRODUCTION

Aspirin (acetylsalicylic acid) is a type of non-steroidal anti-inflammatory medicine, which is frequently employed to relieve pain and reduce fever. Its use during the recent covid pandemic has been increased to considerable extent. Such over-dose of aspirin will be thrown into the atmosphere without metabolism, which generally pollute the natural water resources. Advanced oxidation [1] as well as electrochemical oxidation [2-4] have been proposed to degrade the unmetabolized aspirin in order to clean the biological effluents. Mechanism of reactions of aspirin with various oxidants in both alkaline [5-9] and acidic [10-14] medium have also been studied to understand the probable pathway of generation of the end products. Aspirin undergo hydrolysis [15,16] through uncatalyzed and acid as well as alkali catalyzed mechanism leading to the formation of salicylic acid. Therefore, in most of the oxidation studies of aspirin, salicylic acid is considered as the main substrate, which interact with the oxidant. The salicylic acid also act as a bidentate ligand for Fe^{3+} [17] whereas unhydrolyzed aspirin as a monodentate ligand for Pt^{4+} [18] and transition metal ions [19]. Therefore, the mild oxidants like Fe^{3+} [17] and Pt^{4+} [18] with redox potentials of 0.783 V and 0.68 V, respectively form stable complexes with either salicylic acid or aspirin. The strong oxidants like colloidal MnO_2 [10] and Ce^{4+} [11] oxidize aspirin to the end product generally benzoquinone.

Heteropolyoxometalates (HPOs) with transition metal ions in their higher oxidation states are considered as one of the best

examples of outer-sphere reagents [20]. They are also involved in the multiple protonation equilibria due to high negative charge thus making them as good acid catalysts [21-23]. The higher Brønsted acidity of HPOs is comparable with that of mineral acids. In the present study, enneamolybdomanganate(IV) ($Mn^{IV}Mo_9O_{32}^{6-}$) is used as an oxidant for aspirin and salicylic acid in perchloric acid medium. As mentioned earlier aspirin undergo hydrolysis [15,16] in presence of an acid and the oxidant is $H_6Mn^{IV}Mo_9O_{32}$ is hexaprotonated with dissociable protons thus making it as a strong acid [21-23]. Therefore, in order to understand, during oxidation of aspirin by $Mn^{IV}Mo_9O_{32}^{6-}$, both its acidic and oxidant efficiency the present study was carried out. Fortunately, the hydrolyzed product of aspirin, salicylic acid, does not undergo further acid catalyzed hydrolysis so that both acid and oxidation characteristics of $H_6Mn^{IV}Mo_9O_{32}$ can be separately studied. Therefore, we reports here the oxidation of aspirin and salicylic acid to arrive at probable mechanisms of both the substrates.

EXPERIMENTAL

All chemicals were of reagent grade and the double-distilled water was used throughout the work. Aspirin and salicylic acid were purchased from TCI and E. Merck, respectively and their solutions were freshly prepared by dissolving an appropriate amount of sample in AR grade dimethyl sulfoxide (SRL). Standard solution of perchloric acid (AR, Loba) was prepared in double-distilled water. The sodium perchlorate used to maintain the ionic strength was prepared by neutralizing perchloric acid by sodium hydroxide.

Synthesis and characterization of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$: The ammonium salt of Mn^{IV} complex, $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was prepared by reported method [24], In brief, 50 g of ammonium molybdate was dissolved in 200 mL of water and excess of hydrogen peroxide as oxidant was added to it and the resultant solution was heated to 95 ºC. To this hot solution, 5 g of $MnSO_4 \cdot H_2O$ in 50 mL of water was added slowly with constant stirring. The resultant orange-red coloured solution was boiled for 10 min and quickly filtered and cooled. The orange-red coloured crystals were recrystallized from hot water (70 ºC). The solution of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was standardized by treating known amount of complex solution with excess of As^{III} and back titrating As^{III}. The oxidation state of hetero-atom was also confirmed to be four by iodometric method.

The complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]\cdot 3H_2O$, was analyzed by AAS. The solution for AAS analysis was prepared by dissolving 100 mg of recrystallized sample in double distilled water and 5 mL of this stock solution was diluted to 100 mL. The diluted solution was used for AAS analysis of Mn and Mo using Perkin-Elmer AAnalyst-300 instrument. The complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]\cdot 3H_2O$ shows found (calcd.) %: Mn, 3.501 (3.449) and Mo: 54.217% (54.213%).

The FTIR spectra of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ complex was taken in KBr by using Jasco FTIR-4600 spectrometer. The complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ contains Mn^{IV} as a hetero-atom surrounded by octahedral groups of MoO_6^{2-}. In Mn^{IV} complex (Fig. 1), the peaks obtained at 3135, 1400 cm^{-1} correspond to NH_4^+ ions, 3527, 3135 and 1606 cm^{-1} correspond to O-H and H-O-H, 934 and 899 cm^{-1}, correspond to Mo-Ot, 593 and 419 cm^{-1} correspond to Mo-Ob-Mo and Mn-O and Mn-O-Mo appear at 540 and 492 cm^{-1}, respectively [24,25].

Kinetic measurements: Kinetic measurements were performed on Systronics VISIBLE-SPECTRO 105 spectrophotometer. The kinetics was followed under pseudo-first order conditions, where [substrate] > [oxidant] at constant temperature 30 ± 0.1 ºC. The reaction was initiated by mixing the previously thermostated solutions of either aspirin or salicylic acid and $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$, which also contained the required amount of perchloric acid and double distilled water. The progress of reaction was followed spectrophotometrically at 470 nm by monitoring the decrease in absorbance of oxidant. The pseudo-first order rate constants were determined from the log [Abs] *versus* time plots.

RESULTS AND DISCUSSION

Reaction stoichiometry: The stoichiometry was studied by keeping concentration of $[Mn^{IV}Mo_9O_{32}]^{6-}$ constant at 4.0×10^{-3} mol dm^{-3} and varying concentration of aspirin and salicylic acid from 1×10^{-3} to 2×10^{-4} mol dm^{-3} these reaction mixtures also contained required amount of perchloric acid. The concentration of unreacted $[Mn^{IV}Mo_9O_{32}]^{6-}$ was determined up to a

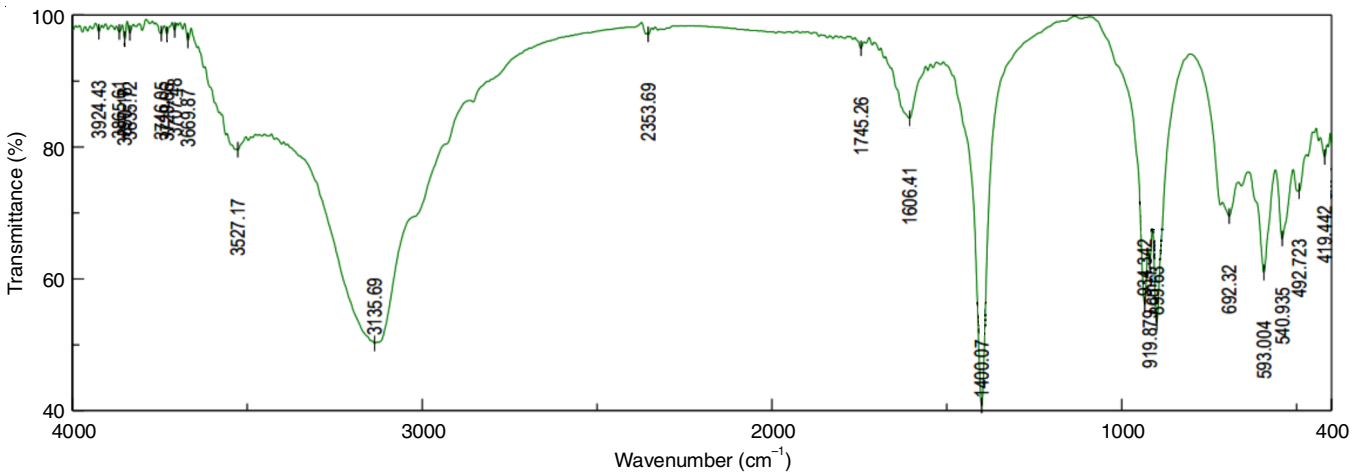
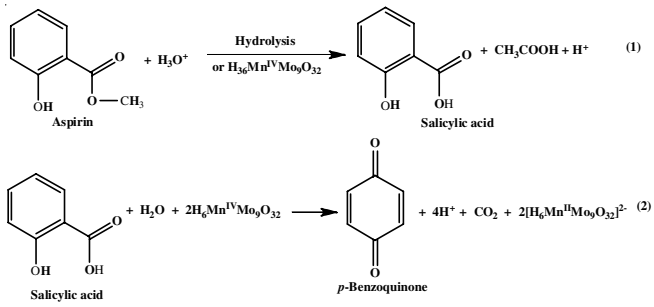


Fig. 1. FTIR spectrum of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ complex

week after each 24 h spectrophotometrically till the absorbance value is constant. The stoichiometry was found to be two moles of $[Mn^{IV}Mo_9O_{32}]^{6-}$ per mole of each aspirin and salicylic acid. Further, the reaction mixture containing 4.0×10^{-3} mol dm^{-3} of $[Mn^{IV}Mo_9O_{32}]^{6-}$ and excess of either aspirin or salicylic acid (1.3×10^{-2} mol dm^{-3}) was kept undisturbed up to 72 h. The reaction mixture was neutralized with NaOH and filtered. The yellow filtrate was extracted with petroleum ether and dried with anhydrous Na_2SO_4. The solvent was evaporated and its FTIR spectrum was recorded in nujol mull with Perkin-Elmer AAnalyst-300 instrument. The FTIR spectrum shows peaks at 1633, 1473 cm^{-1} corresponding to C=O groups and 1216 cm^{-1} to of benzene ring of *p*-benzoquinone [26], respectively (Fig. 2). Therefore, from the spectrophotometric analysis and FTIR spectrum the stoichiometry of the reaction can be given as in eqn. 2.



Reaction order: The reaction was carried out under pseudo first-order conditions, keeping the concentration of $HClO_4$ constant at 0.46 mol dm^{-3} and varying either [substate] from 0.2×10^{-2} to 2.0×10^{2} mol dm^{-3} at constant $[Mn^{IV}Mo_9O_{32}]^{6-}$ (4.0×10^{-4} mol dm^{-3}) or $[Mn^{IV}Mo_9O_{32}]^{6-}$ from 2.0×10^{-4} to 8.0×10^{-4} mol dm^{-3} at constant [substrate] (1.0×10^{-2} mol dm^{-3}) (Table-1). The pseudo first-order plots of log abs. against time in case of aspirin were found to be linear indicating the order with respect to the [oxidant] is unity. The pseudo first-order rate constants were found to be increase with increase in the concentration of both the substrates (Table-1) indicating first order dependence of the reaction on their concentration. The pseudo first-order plots were found to be linear indicating the order in oxidant $[Mn^{IV}Mo_9O_{32}]^{6-}$ is found to be unity. The pseudo

TABLE-1
EFFECT OF H_6 $[Mn^{IV}Mo_9O_{32}]$, [SUBSTRATE]* and [HCl] ON THE PSEUDO-FIRST-ORDER RATE CONSTANT, k_{obs} AT 303.15 K (I = 1.0 mol dm^{-3})

10^4 $[Mn^{IV}Mo_9O_{32}]^{6-}$ (mol dm^{-3})	10^2 [Substrate] (mol dm^{-3})	$[HClO_4]$ (mol dm^{-3})	10^4 k (s^{-1})	
			Aspirin	Sal
2.0	1.0	0.5	1.02	0.80
3.0	1.0	0.5	1.75	0.82
4.0	1.0	0.5	2.05	0.81
5.0	1.0	0.5	2.70	0.82
6.0	1.0	0.5	3.30	0.80
7.0	1.0	0.5	3.80	0..81
8.0	1.0	0.5	4.41	0.80
4.0	0.2	0.5	0.48	0.20
4.0	0.5	0.5	0.90	0.35
4.0	1.0	0.5	2.02	0.81
4.0	1.5	0.5	2.90	1.16
4.0	2.0	0.5	4.10	1.64
4.0	1.0	0.1	0.27	0.79
4.0	1.0	0.2	0.58	0.80
4.0	1.0	0.5	2.02	0.81
4.0	1.0	0.8	2.94	0.82
4.0	1.0	1.0	3.63	0.82

*Substrate is either aspirin or salicylic acid

first-order rate constant values remain constant as $[Mn^{IV}Mo_9O_{32}]^{6-}$ increases for salicylic acid while they increase for aspirin (Table-1). The plot of k_{obs} against $[Mn^{IV}Mo_9O_{32}]^{6-}$ was found to be linear (Fig. 3) indicating the first order dependence of oxidant apart form the first order obtained during pseudo first-order plots.

The effect of hydrogen ion concentration on the reaction was studied in order to understand the nature of reactant species present in the solution. The $[HClO_4]$ was varied from 0.1 to 1.0 mol dm^{-3} keeping all other concentrations constant. It was found that the values of k_{obs} increases with the $[H^+]$ ions for aspirin, whereas they remain constant for salicylic acid (Table-1).

Interference of free radicals and effect of tetrasodium pyrophosphate: The reaction was also studied in presence of added acrylonitrile to understand the intervention of free radicals [27]. There was no effect of added acrylonitrile on the reaction and no precipitate due to the polymerization of the added acrylonitrile was observed thus confirming the absence of any free radical formation in the reaction. Interference of Mn(III) was

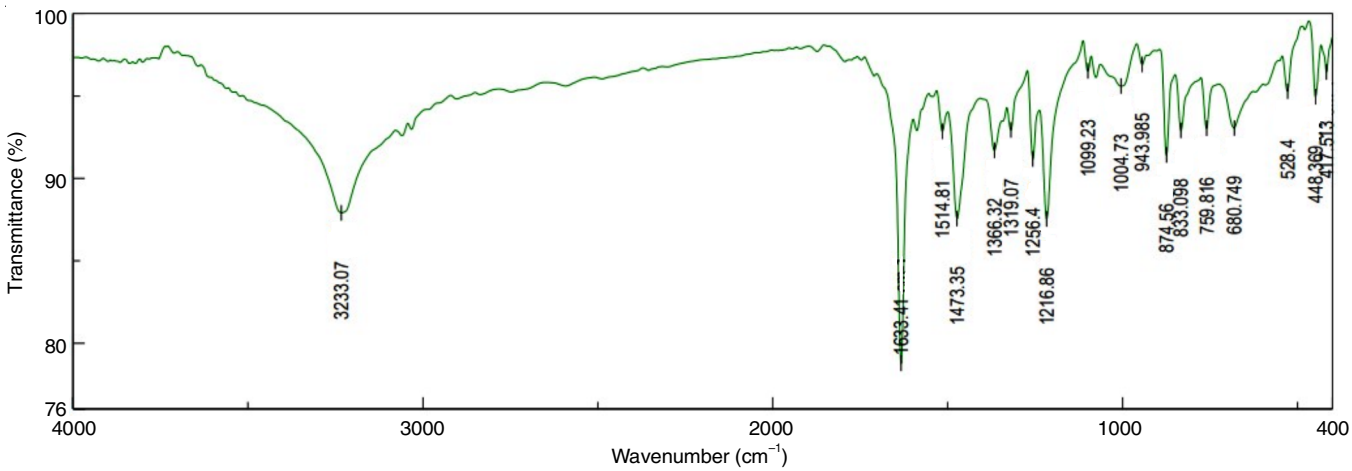


Fig. 2. FTIR spectrum of product of reaction *p*-benzoquinone

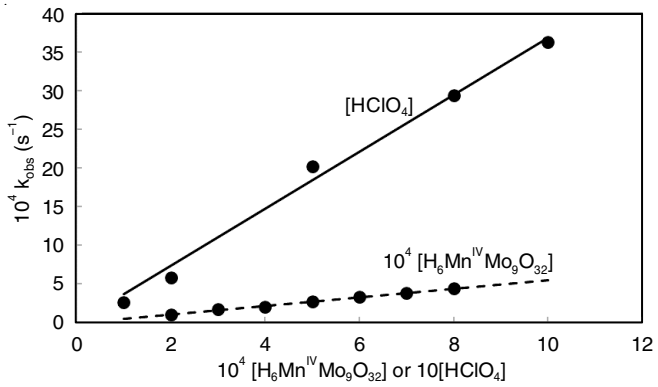


Fig. 3. Plot of k_{obs} against [$H_6Mn^{IV}Mo_9O_{32}$] and [$HClO_4$] for oxidation of aspirin by $H_6[Mn^{IV}Mo_9O_{32}]$; verification of rate law (10) (conditions as in Table-1)

also studied by adding excess of tetrasodium pyrophosphate. The k_{obs} values remain unaffected by the addition of tetrasodium pyrophosphate indicating no interference of Mn(III) in the reaction, which also support the effect of acrylonitrile on the reaction.

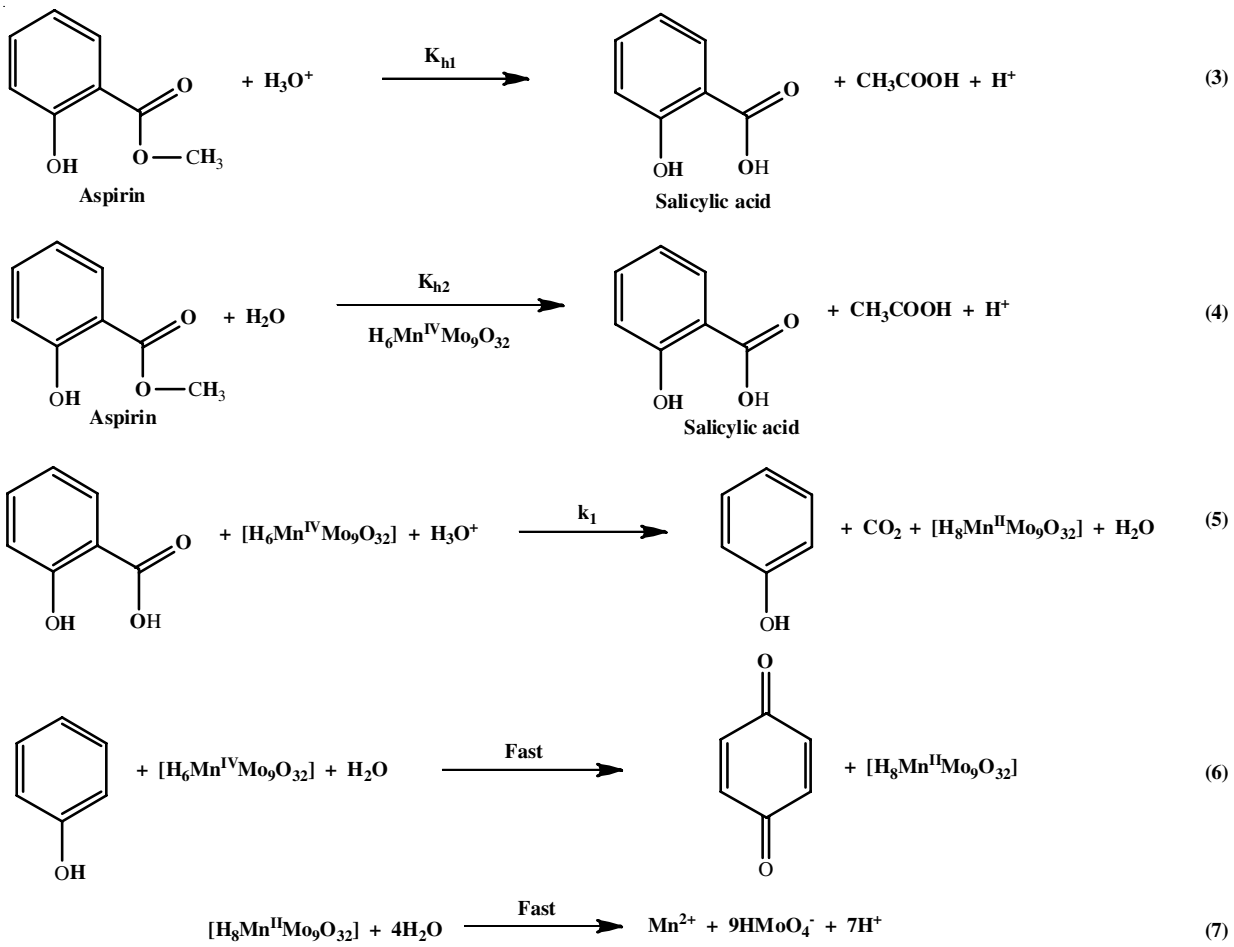
Effect of ionic strength, solvent polarity, temperature and added products: The effects of ionic strength and solvent polarity were studied keeping concentration of $[Mn^{IV}Mo_9O_{32}]^{6-}$, substrates and $HClO_4$ constant of 4.0×10^{-4} mol dm^{-3}, 0.01 mol dm^{-3} and 0.5 mol dm^{-3}, respectively at 30 ºC. Sodium perchlorate was used to vary the ionic strength. The rate of the reaction was unaffected with varying ionic strength from 0.5 to 1.0 mol dm^{-3} and the rate of reaction increases as percentage of acetonitrile increase from 0 to 40% v/v. The plot of log k_{obs} *vs.* 1/D is with negative slope. This decrease in rate with decrease in the dielectric constant is in conformity with Amis concept [27] for ion-dipole interactions. The added products $Mo_7O_{24}^{6-}$ and Mn^{2+} did not have any effect on the values of k_{obs}. The effect of temperature was studied at 10, 20, 25, 30 and 40 ºC and the activation parameters were determined (Table-2).

The effect of oxidant, $[Mn^{IV}Mo_9O_{32}]^{6-}$, on the oxidation of aspirin and salicylic acid indicate that the order in oxidant is unity as the pseudo-first-order plots were linear in both cases. In case of aspirin, the values of k_{obs} increases linearly with the [$H_6Mn^{IV}Mo_9O_{32}$] while the values remain unaffected for salicylic acid (Table-1). The aspirin is known to undergo hydrolysis [15,16] in aqueous solutions, which is catalyzed by both acid and alkali. The present study was carried out in acidic perchloric acid solution therefore, acid catalyzed hydrolysis is the initial step of the mechanism during oxidation of aspirin. The heteropolyacids like $[Mn^{IV}Mo_9O_{32}]^{6-}$ will have Brønsted acidity [21-23] comparable or even more than that of the mineral acids and have been utilized for various acid catalyzed organic transformations [28]. Therefore, the oxidation of aspirin is initiated by acid catalyzed hydrolysis step, which will be absent for that of salicylic acid. The rate constant for the acid catalyzed hydrolysis of aspirin around pH 0.5 is reported to be of the order of 10^{-5} s^{-1} [15,16]. Whereas, the values of k_{obs} for the oxidation of aspirin were found to be of the order 10^{-4} s^{-1} (Table-1), which is more than the hydrolysis in acidic medium. The values of k_{obs} for the oxidation of salicylic acid under identical conditions are also of the same order. Therefore, the oxidation of both the substrates is actually the oxidation of salicylic acid. The accelerating effect of $[Mn^{IV}Mo_9O_{32}]^{6-}$ for aspirin also indicate that apart from the role of oxidant, it also helps for the hydrolysis as an acid catalyst. Therefore, $[Mn^{IV}Mo_9O_{32}]^{6-}$ acts both as an acid catalyst and as an oxidant for the oxidation of aspirin. The effect of [substrates], both aspirin and salicylic acid, on the values of k_{obs} increases indicating a first order dependence of the reaction on [substrate].

The increasing [$HClO_4$] did not affect the values of k_{obs} for salicylic acid while there is increase in the values of k_{obs} for aspirin (Table-1). As mentioned earlier, the product of hydrolysis of aspirin is salicylic acid, which has dissociable carboxylic acid proton and its p*K* value is reported [29] to be 3.1. Since, the minimum [$HClO_4$] used in the present study is 0.1 mol dm^{-3} the carboxylic group of salicylic acid is completely protonated. Similarly, the oxidant, $[Mn^{IV}Mo_9O_{32}]^{6-}$, is also in the completely protonated form [30]. The increase in the values of k_{obs} in case of aspirin is due the increase in the rate of its hydrolysis. During oxidation of many inorganic and biologically important molecules, $[Mn^{IV}Mo_9O_{32}]^{6-}$ was found to be a two electron transfer outer sphere reagent [31-34]. The general mechanism in all these oxidations involve formation of a precursor complex with hexaprotonated, [$H_6Mn^{IV}Mo_9O_{32}$], as the active oxidant species. The possibility of intervention of free radical as a result of one electron transfer generating Mn(III) is also verified by studying the reaction in presence of acrylonitrile and tertrasodium pyrophosphate. The values of rate constants remain unaffected in presence of acrylonitrile and tetrasodium pyrophosphate as well as no precipitation was observed due to the polymerization of acrylonitrile for both aspirin and salicylic acid. These results indicate that both the substrates react with the oxidant and involve two electron transfer without intervention of a free radical and Mn(III). Therefore, a general mechanism for aspirin and salicylic acid can be represented by **Scheme-I**.

TABLE-2
EFFECT OF TEMPERATURE AND VALUES OF ACTIVATION PARAMETERS FOR OXIDATION OF ASPIRIN AND SALICYLIC ACID BY H_6 [$Mn^{IV}Mo_9O_{32}$]
(10^4 [$H_6[Mn^{IV}Mo_9O_{32}]$] = 4.0 mol dm^{-3}, 10^2 [ASP] = 1.0 mol dm^{-3} and [$HClO_4$] = 0.5 mol dm^{-3} and I = 1.0 mol dm^{-3})

Temperature (K)	10^4 k_{obs} (s^{-1})			Aspirin	Salicylic acid
	Aspirin	Salicylic acid			
283.15	0.42	0.41	E_a (kJ mol^{-1})	47.1	28.7
293.15	0.78	0.60	$\Delta H^{\#}$ (kJ mol^{-1})	45.8	26.3
298.15	1.50	0.70	$\Delta G^{\#}$ (kJ mol^{-1})	82.2	81.2
303.15	2.05	0.81	$-\Delta S^{\#}$ (J $K^{-1}mol^{-1}$)	120	181
313.15	2.55	1.37			



Scheme-I: Proposed mechanism of oxidation of aspirin and salicylic acid by $[H_6Mn^{IV}Mo_9O_{32}]$

According to **Scheme-I**, the initial hydrolysis of aspirin occurs in presence of $HClO_4$ as well as $[H_6Mn^{IV}Mo_9O_{32}]$ with corresponding hydrolysis constants K_{h1} and K_{h2} as represented by eqns. 3 and 4, respectively. Both hydrolysis steps generate the salicylic acid, which will be the substrate for next subsequent steps. Decarboxylation of salicylic acid occurs by the reaction of an oxidant in a rate determining step followed by formation of *p*-benzoquinone in a fast step. These reactions are represented by eqns. 5 and 6, respectively. The final product of oxidant $[H_8Mn^{II}Mo_9O_{32}]$ is unstable, which decomposes to Mn^{2+} and $HMoO_4^-$ ions as shown by eqn. 7 of **Scheme-I**. The rate of the reaction is given by eqn. 8 and considering both hydrolysis steps 3 and 4, we get eqn. 9. Rearranging eqn. 9 leads to the expression 10 for the k_{obs} value. According to eqn. 10 plots of k_{obs} against $[H_6Mn^{IV}Mo_9O_{32}]$ and $[HClO_4]$ were found to be linear (Fig. 3) and the slopes gives the values of k_1K_{h1} and k_2K_{h2}, respectively. These values of the k_1K_{h1} and k_2K_{h2} were found to be 5.45×10^{-5} s^{-1} and 3.68×10^{-4} s^{-1}, respectively indicating that the hydrolysis is much faster in presence of $HClO_4$ than that of $[H_6Mn^{IV}Mo_9O_{32}]$.

$$\text{Rate} = k_1[H_6Mn^{IV}Mo_9O_{32}][\text{Salicylic acid}] \quad (8)$$

$$\text{Rate} = k_1(K_{h1}[H^+] + K_{h2}[H_6Mn^{IV}Mo_9O_{32}])[\text{Aspirin}][H_6Mn^{IV}Mo_9O_{32}] \quad (9)$$

$$k_{obs} = \text{Rate}/[H_6Mn^{IV}Mo_9O_{32}] = k_1(K_{h1}[H^+] + K_{h2}[H_6Mn^{IV}Mo_9O_{32}])[\text{Aspirin}] \quad (10)$$

Since, the oxidation aspirin is initiated by the generation of salicylic acid, which is the substrate for further reactions then the steps 5 to 7 are applicable to the salicylic acid oxidation. The rate law in case of salicylic acid would be given by eqn. 11 with corresponding expression for k_{obs} by eqn. 12.

$$\text{Rate} = k_1[H_6Mn^{IV}Mo_9O_{32}][\text{Salicylic acid}] \quad (11)$$

$$k_{obs} = \text{Rate}/[H_6Mn^{IV}Mo_9O_{32}] = k_1[\text{Salicylic acid}] \quad (12)$$

The effect of solvent polarity on the reaction indicating that there is decrease in the values of k_{obs} as the dielectric constant (D) decreases for both aspirin and salicylic acid. The plot of log k against (1/D) is linear with a negative slopes for both aspirin and salicylic acid. The effect of solvent can be explained by using Amis concept that the reaction between either negative ion-dipole or two dipoles a plot of log k against (1/D) gives a straight line with negative slope [35]. The activation parameters for both the reactions were determined by studying the reaction at 10, 20, 25, 30 and 35 ºC and the data are given in Table-2. The values of E_a and $\Delta H^{\#}$ were found to be higher for aspirin than that for the salicylic acid (Table-2). The reported values E_a and $\Delta H^{\#}$ of for hydrolysis [15] of aspirin are about 70 kJ mol^{-1}. The values determined in the present study for oxidation of aspirin are about 50 kJ mol^{-1}. Although the values are lesser that that of the hydrolysis of aspirin, which might be due to the additional oxidant assisted hydrolysis as shown by eqn. 4

of **Scheme-I**. On the other hand, the $\Delta S^{\#}$ value for aspirin is lesser negative than that for salicylic acid. The value of $\Delta S^{\#}$ = -110 J K^{-1} mol^{-1} for hydrolysis [15] is comparable to that obtained -120 J K^{-1} mol^{-1} for its oxidation in the present study. Therefore, the conclusion of initial hydrolysis of aspirin and oxidant assisted hydrolysis while proposing the mechanism of **Scheme-I** is justifiable. The higher negative value of $\Delta S^{\#}$ = 181 J $K^{-1}mol^{-1}$ for salicylic acid is in support of **Scheme-I** due to prior weak precursor complex formation between the reactants as observed in earlier reports. Once the reorganization energy required for the formation a weak precursor complex between the reactants is acquired by them, for hydrolysis in case of aspirin and direct oxidation in case of salicylic acid, the difference in the activation energy would be lesser as observed in the values of $\Delta G^{\#}$, which were found to be around 82 kJ mol^{-1} (Table-2).

Conclusion

The oxidation of aspirin and salicylic acid by enneamolybdomanganate(IV) were studied in perchloric acid medium. The key step of the proposed mechanism involved the oxidation of salicylic acid by enneamolybdomanganate(IV). Salicylic acid is generated as a result of hydrolysis of aspirin, which was found to be catalyzed by both $HClO_4$ and the oxidant. The rate constant for the hydrolysis of aspirin catalyzed by $[H_6Mn^{IV}Mo_9O_{32}]$ was found to be lesser than that in for $HClO_4$. A weak prior complex formation is formed between reactants leading to low negative activation entropy. The rate law for aspirin was verified by plotting k_{obs} against both $[H_6Mn^{IV}Mo_9O_{32}]$ and $[HClO_4]$ the reactants while for salicylic acid, due to absence of hydrolysis step, a simple rate law was resulted. The effect of solvent polarity on the reaction indicates reaction between two dipoles. The mechanism for both aspirin and salicylic acid involves direct two electron transfer reaction without any intervention of either free radicals or Mn(III). The activation parameters (E_a and $\Delta H^{\#}$) determined were higher for aspirin due to initial oxidant assisted hydrolysis step. The product of reaction *p*-benzoquinone was characterized by FTIR and formed in two steps. The decarboxylation of salicylic acid occurs generating phenol in a slow step, which then gives the final product in a fast step.

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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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