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Oxidation of *para*-Methoxy Benzaldehyde and Salicylaldehyde by N-Sodio-N-Chlorotoluene Sulphonamide (Chloramine-T) in Acid Medium: A Kinetic and Mechanistic Study

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The kinetics of oxidation of *para*-methoxy benzaldehyde and salicylaldehyde by chloramine-T (CAT) have been investigated in hydrochloric acid medium at 303 K. The rate shows first order dependence on [CAT] and fractional order in [aldehyde]. The rate increases with increase in [HCl] and shows first order dependence on [H^+] and [Cl^-], variation of ionic strength, addition of reaction product (*para*-toluene sulphonamide) and change in dielectric constant of the medium had no significant effect on the reaction rate. Thermodynamic parameters are evaluated.

INTRODUCTION

Ru(III) catalyzed oxidation of benzaldehyde and substituted benzaldehydes by HIO_4, sodium metaperiodate, and OsO_4 catalyed oxidation in alkaline hexacyano ferrate(III) also by N-bromosuccinimide, permonosulphate, 1-chlorbenzotriazole have been studied[1–6]. In our previous publication[7], oxidation of *p*-methoxy benzaldehyde (PMB) and salicylaldehyde (SA) by chloramine-B has been reported. In the present paper we report the mechanistic and kinetic aspects of oxidation of the above aldehydes by chloramine-T (CAT) (CH_3-$C_6H_4SO_2NClNa\cdot 3H_2O$) in hydrochloric acid medium at 303 K.

RESULTS AND DISCUSSION

The kinetics of oxidation of *para*-methoxy benzaldehydes and salicylaldehyde by CAT was investigated in 30% ethanol medium. Blank experiments with ethanol, however, showed that there is slight reaction of the solvent (less than 3%) under the experimental conditions used. This was allowed in the calculation of net reaction rate constant for the oxidations of aldehydes.

Stoichiometry and product analysis: Stoichiometric experiments show that one mole of the aldehydes consume one mole of the oxidant under experimental conditions and given by Eqn. (1).

$$RCHO + R'NClNa + H_2O \xrightarrow{\qquad} RCOOH + NaCl + R'NH_2 \qquad (1)$$

Here $R = OCH_3C_6H_4$ for *para*-methoxy benzaldehyde

$R = OHC_6H_4$ for salicylaldehyde

$R' = CH_3C_6H_4SO_2$

Para-toluene sulphonamide ($CH_3C_6H_4SO_2NH_2$) was detected[8] by thin layer chromatography using solvent system of benzyl alcohol saturated with water and 0.5% vanillin in 1% HCl in ether as spray reagent ($R_f = 0.905$). The other product was identified as acid by conventional neutral ferric chloride test.

Effect of reactants: With the substrate in excess, at constant [HCl] and $[\text{aldehydes}]_0$ plot of log [CAT] *vs.* time were linear ($r > 0.999$) indicating first order dependence of the rate on [CAT]. The pseudo-first order rate constant (k′) is given in Table-1. A plot of log k′ *vs.* log $[\text{aldehydes}]_0$ was linear ($r > 0.996$) with fractional slope indicating fractional order dependence on the [aldehydes] (Table-1, Fig. 1).

TABLE-1
EFFECT OF VARYING REACTANT CONCENTRATIONS ON THE RATE OF REACTION

10^3 [CAT] (mol dm^{-3})	10^2 [PMB] (mol dm^{-3})	10^2 [SA] (mol dm^{-3})	PMB $k' \times 10^4$ (s^{-1})	SA $k' \times 10^4$ (s^{-1})
1.6	4.0	4.0	2.00	11.61
1.8	4.0	4.0	1.96	11.44
2.0	4.0	4.0	2.06	11.52
2.2	4.0	4.0	2.10	11.50
2.5	4.0	4.0	2.13	44.58
2.0	2.0	2.0	1.71	9.20
2.0	4.0	4.0	2.06	11.52
2.0	6.0	6.0	2.24	13.25
2.0	8.0	8.0	2.58	14.56
2.0	10.0	10.0	2.75	15.67
2.0	12.0	12.0	2.91	16.63
2.0	15.0	15.0	3.11	17.89

[HCl] = 0.1 mol dm^{-3}, μ = 0.4 mol dm^{-3}, Temperature = 303 K

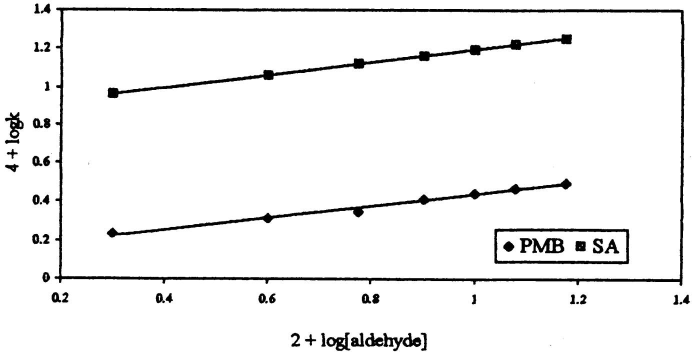

Fig. 1. Plot of log k′ *vs.* log [aldehyde]

Effect of [H^+]: The rate of reaction increased with increase in [H^+] (5.0×10^{-2} to 20.0×10^{-2} mol dm^{-3}) at constant [Cl^-] (20.0×10^{-2} mol dm^{-3}). The plot of log k′ *vs*. log [H^+] was linear ($r > 0.997$) with slope equal to unity, indicated first order dependence on [H^+] (Table-2, Fig. 2).

Effect of [Cl^-]: The reaction rate increased with increase in [Cl^-] (5.0×10^{-2} to 25.0×10^{-2} mol dm^{-3} by adding NaCl at constant [H^+]). A plot of log k′ *vs*. log [Cl^-] was linear ($r > 0.998$) with slope equal to unity, indicating first order dependence on [Cl^-]. (Table-2, Fig. 2).

TABLE-2

EFFECT OF VARYING [H^+] AND [Cl^-] ON THE RATE OF REACTION

$10^2[H^+]$ (mol dm^{-3})	$k' \times 10^4$ (s^{-1})		10^2 [Cl^-] (mol dm^{-3})	$k' \times 10^4$ (s^{-1})	
	PMB	SA		PMB	SA
2.5	1.29	7.60	15.0	2.51	16.80
5.0	2.58	15.58	20.0	3.10	21.60
10.0	5.15	31.14	25.0	4.03	29.16
15.0	7.72	46.55	30.0	5.16	36.00
20.0	10.31	62.21	35.0	6.12	42.90
25.0	12.89	77.76	–	–	–

[CAT] = 2.0×10^{-3}, $\mu = 0.4$ mol dm^{-3}, [aldehydes] = 0.04 mol dm^{-3}; T = 303 K

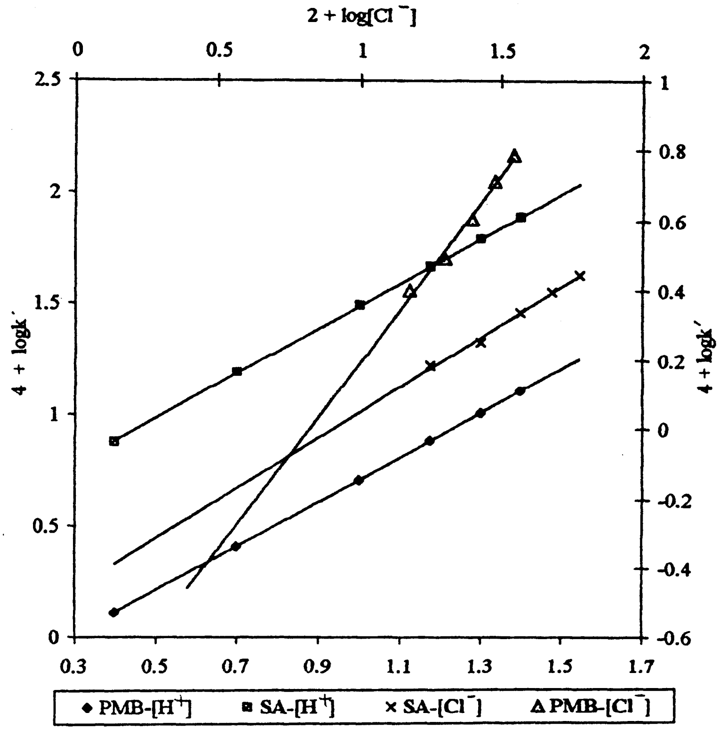

Fig. 2. Plot of log k′ *vs*. log [H^+] and log [Cl^-]

Effect of *para*-toluene sulphonamide on rate: The addition of the reaction product toluene sulphonamide ($CH_3C_6H_4SO_2NH_2$) (1×10^{-3} to 4×10^{-3} mol dm^{-3}) had no influence on the rate of reaction.

Effect of ionic strength and dielectric constant of the medium: The reaction rate remained unaffected on varying ionic strength of the medium by adding sodium perchlorate (0.1 to 0.5 mol dm^{-3}). The solvent composition was varied by adding ethanol (30 – 45% v/v but no significant change in the rate was noticed with increase in ethanol content of the reaction medium.

Effect of temperature: The reaction was studied at different temperatures in the range 298–313K and the values of k′ were determined (Table-3) from the pseudo-first order plots. The activation parameters were calculated from the Arrhenius plot of log $k'V_s 1/T$($r > 0.999$). These are shown in (Table-3).

TABLE-3
KINETIC AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF PMB AND SA BY CAT IN PRESENCE OF HYDROCHLORIC ACID

Temperature (K)	$k' \times 10^4 (s^{-1})$		Parameters	PMB	SA
	PMB	SA			
303	2.06	11.52	E_a(kJ $mole^{-1}$)	87.92	48.25
308	2.92	16.60	$\Delta H^{\#}$ (KJ $mole^{-1}$)	85.40	45.73
313	5.60	22.10	$\Delta S^{\#}$ (kJ $mole^{-1}$)	−75.20	−71.90
318	9.66	27.80	$\Delta G^{\#}$(kJ $mole^{-1}$)	108.20	67.50

Test for free radicals: Addition of the reaction mixture to aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of formation of free radical species in the reaction sequence.

Pryde and Sopper[9], Morries *et al.*[10] and Bishop and Jennings[11] have shown the existence of similar equilibria in acid and alkaline solution of N-metallo-N-haloaryl sulphonamides. Chloramine-T behaves as a strong electrolyte in aqueous solution forming different species as shown in equations (2)–(6)

$$R'NClNa \rightleftharpoons R'NCl^- + Na^+ \quad (2)$$

$$R'NCl^- + H^+ \rightleftharpoons R'NHCl \quad (3)$$

$$R'NHCl + H_2O \rightleftharpoons R'NH_2 + HOCl \quad (4)$$

$$2R'NHCl \rightleftharpoons R'NH_2 + R'NCl_2 \quad (5)$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+ \quad (6)$$

In acid medium, the probable oxidizing species are free acid (RNHCl), dichloramine-T ($R'NCl_2$), HOCl and H_2OCl^+. The involvement of $R'NCl_2$ in the mechanism leads to a second order rate law, according to Eqn. (5), which is contrary to experimental observation. As Eqn. (4) indicates a slow hydrolysis, if HOCl were the primary oxidizing species, a first order retardation of the rate by the added $R'NH_2$ would be expected. However, no such effect was noticed in this study. Hardy and Johnston[12] who have studied the pH dependent relative concentrations of the species present in acidified haloamine solutions of comparable molarities have shown that R′NHCl is the likely oxidizing species in acid medium. Narayanan and Rao[13] and Subhashini *et al.*[14] have reported that monohaloamines can be further protonated at pH < 2 as shown in eqn. (7).

$$p\text{-}CH_3C_6H_4SO_2NHCl + H^+ \rightleftharpoons p\text{-}CH_3C_6H_4SO_2N^+H_2Cl \qquad (7)$$

Therefore, in the present investigation the increase of rate by H^+ indicates the protonation of the species R′NHCl, which is the active oxidizing species. Further, the experiments showed fractional order dependence on $[\text{aldehydes}]_0$ and first order dependence in $[H^+]$ and $[Cl^-]$. In view of above facts Scheme-1 is proposed for the oxidation of aldehydes by CAT.

Scheme-1

$$R'NHCl + H^+ + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(X)}{R'\overset{+}{N}H_2Cl \ldots Cl} \quad \text{(fast)} \qquad (8)$$

$$X + S \xrightarrow{k_2} \text{Products (slow and r.d.s.)} \qquad (9)$$

Scheme-1 leads to the rate law:

$$\text{Rate} = \frac{k_1k_2[\text{CAT}][H^+][Cl^-][S]}{k_{-1} + k_2[S]} \qquad (10)$$

which is in agreement with the experimental results with first order dependence on [CAT], $[H^+]$ and $[Cl^-]$, fractional order dependence on $[\text{aldehydes}]_0$.

The observed values of kinetic and thermodynamic parameters supports the rate mechanism and the fairly high negative value of $\Delta S^{\#}$ indicates the formation of rigid transition state by an associative process.

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