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

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

INTRODUCTION

Oxidation of aldehydes, in particular of aliphatic aldehydes by N-haloamines in acid medium, has already been reported[1–6]. However, there is meagre information about the oxidation of aromatic aldehydes. Therefore, in the present paper, we report the mechanistic and kinetic aspects of oxidation of *para*-methoxy benzaldehyde and salicylaldehyde by chloramine-B (CAB or $C_6H_5SO_2N\cdot ClNa\cdot 1.5H_2O$) in hydrochloric acid medium at 303 K.

RESULTS AND DISCUSSION

The kinetics of oxidation of *para*-methoxy benzaldehyde and salicylaldehyde by CAB 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 oxidation of aldehydes.

Stoichiometry and product analysis: Stoichiometric experiments indicated that one mole of the aldehyde consumed one mole of the oxidant under experimental conditions and given by Eqn. (1).

$$R'CHO + C_6H_5SO_2NClNa + H_2O \longrightarrow R'COOH + NaCl + C_6H_5SO_2NH_2 \quad (1)$$
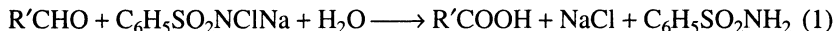
Here $R' = OCH_3C_6H_4$— for *para*-methoxy benzaldehyde (PMB)

and $R' = OHC_6H_4$— for salicylaldehyde (SA).

Benzene sulphonamide ($C_6H_5SO_2NH_2$) was detected by thin layer chromatography using solvent system of petroleum ether-chloroform-1-butanol (2 : 2 : 1 v/v) in ascending irrigation and using iodine vapour as the developing reagent ($R_f = 0.88$)[7]. 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 [aldehyde]$_0$, plots of log [CAB] *vs* time were linear, indicating first order dependence of rate on [CAB]$_0$. The pseudo-first-order rate constants (k') obtained were given in Table-1. A plot of log k' vs. log [aldehyde]$_0$ was linear with fractional slope indicating fractional order dependence on the [aldehyde] (Table-1, Fig. 1).
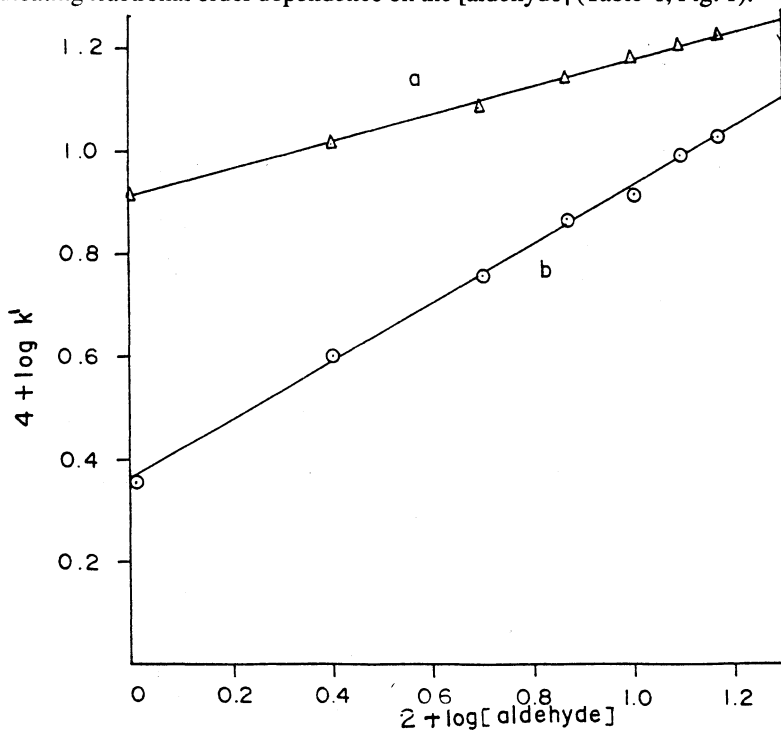

Fig. 1. Plot of log k' *vs* log [aldehyde] (a) salicylaldehyde, (b) *p*-methoxy benzaldehyde

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

10^3 [CAB] (mol dm^{-3})	10^2 [PMB] (mol dm^{-3})	10^2 [SA] (mol dm^{-3})	PMB k' × 10^4 (s^{-1})	SA k' × 10^4 (s^{-1})
1.2	5.0	5.0	5.81	12.38
1.4	5.0	5.0	5.77	12.35
1.6	5.0	5.0	5.72	12.30
1.8	5.0	5.0	5.71	12.28
2.0	5.0	5.0	5.67	12.22
1.6	1.0	1.0	2.24	8.10
1.6	2.5	2.5	3.94	10.50
1.6	5.0	5.0	5.72	12.30
1.6	7.5	7.5	7.41	13.80
1.6	10.0	10.0	8.33	15.10
1.6	12.5	12.5	9.77	15.85
1.6	15.0	15.0	10.68	16.40

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

Effect of (H^+):   The rate of reaction increased with increase in [H^+], at constant [Cl^-]. The plot of log k′ *vs* log [H^+] was linear with slope equal to unity, indicating first order dependence on the [H^+] (Table-2, Fig. 2).
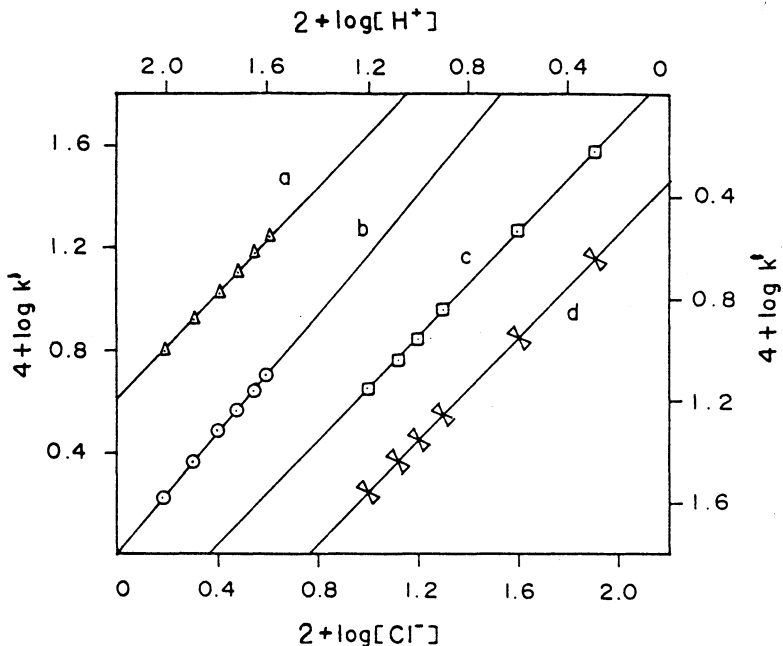

Fig. 2.   Plot of log k′ verses log [H^+]) and log [Cl^-] (a) and (c) *p*-methoxy benzaldehyde, (b) and (d) salicylaldehyde

TABLE-2

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

10^2 [H^+] (mol dm^{-3})	k′ × 10^4 (s^{-1})		[Cl^-] (mol dm^{-3})	k′ × 10^4 (s^{-1})	
	PMB	SA		PMB	SA
2.0	1.70	.50	0.15	6.24	17.10
4.0	3.50	9.20	0.20	8.32	23.60
8.0	7.06	18.00	0.25	10.47	30.70
10.0	9.12	22.91	0.30	12.80	37.10
12.0	10.95	27.40	0.35	15.13	43.50
16.0	14.45	36.30	—	—	—

[CAB] = 1.6 × 10^{-3} mol dm^{-3}, [aldehyde] = 5 × 10^{-2} mol dm^{-3}, μ = 0.4 mol dm^{-3}, T = 303 K.

Effect of [Cl^-]:   The reaction rate increased with an increase in [Cl^-] (by adding NaCl at constant [H^+]) and plot of log k′ vs. log [Cl^-] was linear with slope equal to unity, .showing first order dependence on (Cl^-) (Table-2, Fig. 2).

Effect of benzene sulphonamide on rate: The addition of the reaction product benzene sulphonamide $(C_6H_5SO_2NH_2)$ $(1 \times 10^{-3}$ to 3×10^{-3} mol dm$^{-3})$ had no effect on the rate of reaction.

Effect of ionic strength and dielectric constant of the medium: Variation of ionic strength of the medium by adding NaClO$_4$ (0.1–0.5 mol dm^{-3}) had no effect on the rate. The reaction was studied in aqueous ethanol of different compositions (30–45% v/v) indicating negligible effect on the rate of reaction.
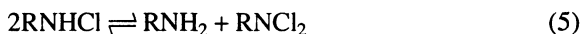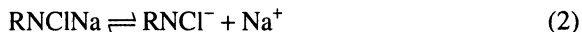
Effect of temperature: The reaction was studied at different temperatures in the range 298–313 K and values of k′ were determined (Table-3) from the pseudo-first-order plots. The energy of activation E_a was calculated from the Arrhenius plot of log k′ *vs* 1/T. The other activation parameters were calculated by making use of the value of E_a (Table-3).

TABLE-3

KINETIC AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF PMB AND SA BY CAB IN PRESENCE OF HYDROCHLORIC ACID

Temperature (K)	PMB $k' \times 10^4$ (s^{-1})	SA $k' \times 10^4$ (s^{-1})	Parameters	PMB	SA
298	3.98	8.32	Ea (kJ mol^{-1})	44.9	62.5
301	4.76	10.50	$\Delta H^{\neq}$ (kJ mol^{-1})	42.4	60.0
303	5.72	12.30	$\Delta S^{\neq}$ (J K mol^{-1})	−167.7	−102.8
306	6.54	16.40	$\Delta G^{\neq}$ (kJ mol^{-1})	93.6	91.3
309	7.57	19.30			
313	9.16	28.20			

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

Pryde and Soper[8], Morries, *et al.*[9] and Bishop and Jennings[10] have shown the existence of similar equilibria in acid and alkaline solutions of N-metallo-N-haloarylsulphonamides. Chloramine-B, being analogus to CAT, behaves as a strong electrolyte in aqueous solutions forming different species as shown in Eqns. (2)–(6)
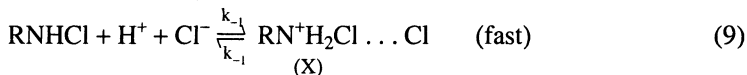
$$RNClNa \rightleftharpoons RNCl^- + Na^+ \qquad (2)$$

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad (3)$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \qquad (4)$$

$$2RNHCl \rightleftharpoons RNH_2 + RNCl_2 \qquad (5)$$

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

In acid solutions, the probable oxidizing species are free acid (RNHCl), dichloramine-B (RNCl$_2$), HOCl and H$_2$OCl$^+$. the involvement of RNCl$_2$ in the mechanism leads to a second order rate dependence on [CAB]$_0$, according to Eqn (5), which is contrary to the experimental observations. As Eqn. (4) indicates a slow hydrolysis, if HOCl were the primary oxidizing species of first order, a

retardation of the rate by the added RNH_2 would be expected. However, no such effect was noticed in this study. Therefore, RNHCl is the likely predominating oxidising species in acid medium. Further, Narayanan and Rao[11] and Subhashini *et al.*[12] have reported that monohaloamines can be further protonated in acid medium, as in Eqns. (7) and (8).

$$p\text{-}CH_3C_6H_4SO_4NHCl + H^+ \rightleftharpoons p\text{-}CH_3C_6H_4SO_2N^+H_2Cl \qquad (7)$$

$$C_6H_5SO_2NHCl + H^+ \rightleftharpoons C_6H_5SO_2N^+H_2Cl \qquad (8)$$

Therefore in the present investigation the increase of rate by H^+ indicates the protonation of the species RNHCl, which is the active oxidising species. Further, the experiments showed first order dependence on (Cl^-) and fractional order dependence on (substrate). In view of above facts the Scheme-1 is proposed for the oxidation of aldehydes by CAB.

Scheme-1

$$RNHCl + H^+ + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RN^+H_2Cl \ldots Cl \qquad (fast) \qquad (9)$$
$$(X)$$

$$X + S \overset{k_2}{\longrightarrow} products \qquad (slow\ and\ r.d.s.) \qquad (10)$$

Scheme-1 leads to rate law:

$$Rate = \frac{k_1 k_2 [CAB][H^+][Cl^-][S]}{k_{-1} + k_2[S]} \qquad (11)$$

which is in agreement with the experimental results with first order dependence on [CAB], fractional order dependence on [aldehyde], first order in $[H^+]$ and $[Cl^-]$.

The observed values of kinetic and thermodynamic parameters support the rate mechanism and the fairly high negative value of $\Delta S^{\neq}$ indicates the formation of rigid transition state.

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