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Hypochlorite Oxidation of Benzaldehydes and Some of the *p*-Substituted Benzaldehydes: A Kinetic Study

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Kinetic studies on the sodium hypochlorite oxidation of some aromatic aldehydes in aqueous acetic acid medium have been studied. The reaction showed first order dependence with respect to substrate and oxidant concentrations. The rate increased with increase in $[H^+]$ with fractional order dependence. Effects of ionic strength and dielectric constant of the medium have been investigated. Exner plots gave good correlation for different *para*-substituted benzaldehydes, which also gave good linear fits according to the Hammet equation.

Key Words: Hypochlorite, Oxidation, Benzaldehyde, *p*-Substituted benzaldehydes, Kinetic.

INTRODUCTION

Kinetic studies on the oxidation of aldehydes with a variety of oxidants have already been reported[1–8]. However, most of these reactions were carried out using powerful oxidants such as permanganate, dichromate, etc. Hypochlorite is an inexpensive, mild and non-polluting oxidant which can be used to oxidise aldehydes to the corresponding carboxylic acids without the involvement of side reactions. Kinetic studies on the hypochlorite oxidation of aromatic aldehydes in aqueous acetic acid media are scanty and hence the present work.

EXPERIMENTAL

Aqueous sodium hypochlorite solution (swimming pool reagent) was of E. Merck quality. The aldehydes used were of AnalaR grade and were further purified by distillation under vacuum. AR grade glacial acetic acid used has been refluxed for 6 h with chromic oxide and acetic anhydride and fractionally distilled before use. Stock solutions of the substrate were prepared in the purified glacial acetic acid as and when required. All other chemicals used were of AnalaR grade. Double distilled water was always used.

The kinetic measurements were made under pseudo first order condition by maintaining [substrate] $\gg$ [oxidant]. Appropriate quantities of the substrate, acetic acid and water, were taken in amber coloured pyrex glass bottle in thermostatic baths. The reaction was initiated by adding requisite amount of thermally equilibrated solution of the oxidant to the above mixture. Aliquots were removed at definite time intervals and the unreacted hypochlorite was estimated by iodometric titration. The rate constants were calculated by the method of least squares.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was established by equilibrating the known concentration of the substrate and excess known concentration of the oxidant in aqueous acetic acid medium. From the values of unreacted hypochlorite concentration it has been found that one mole of the aldehyde reacts with one mole of hypochlorite

$$C_6H_5\,CHO + NaOCl \rightarrow C_6H_5COOH + NaCl$$

The product formed, *viz.*, benzoic acid, was detected and estimated by standard methods.

A plot of log [OCl^-] *vs.* time was linear indicating the first order dependence with respect to the concentration of the oxidant. The observed rate constant (k_{obs}) was found to be the same for different concentrations of the oxidant, under otherwise identical conditions of [substrate], solvent, [H^+], ionic strength, etc. The k_{obs} increased with increase of concentration of the substrate in separate investigations. The plot of log (k_{obs}) *vs.* log [PhCHO] gave a linear curve with slope of unity indicating first order dependence with respect to substrate concentration also. The constancy of k_2 values obtained by dividing k_{obs} with substrate concentrations further supports the first order dependence of the reaction with respect to [aldehyde]. These are shown in Table-1. A 100-fold change (0.002–0.2) in ionic strength had practically no change in the rate coefficient values. The plot of 1/log k against 1/log [substrate] was linear passing through the origin which rules out the possibility of any long-lived intermediate compound during the reaction.

TABLE-1

EFFECT OF [SUBSTRATEJ AND [OXIDANT] ON THE RATE OF OXIDATION OF BENZALDEHYDE

Solvent = 20% (v/v) acetic acid ; Ionic strength: 0.2 mol dm^{-3}; Temperature: 303 K

10^3 [NaOCl] (mol dm^{-3})	10^2 [$C_6H_5CH_3$] (mol dm^{-3})	10^5 k_{obs} s^{-1}	10^3 k_2 dm^3 mol^{-1} s^{-1}
0.4	1.0	5.03	5.03
0.6	1.0	5.00	5.00
0.8	1.0	5.18	5.18
1.0	1.0	5.10	5.10
1.0	1.5	7.71	5.14
1.0	2.0	10.25	5.13
1.0	2.5	12.80	5.12
1.0	3.0	15.35	5.12
1.0	5.0	24.75	4.95
1.0	10.0	49.21	4.92

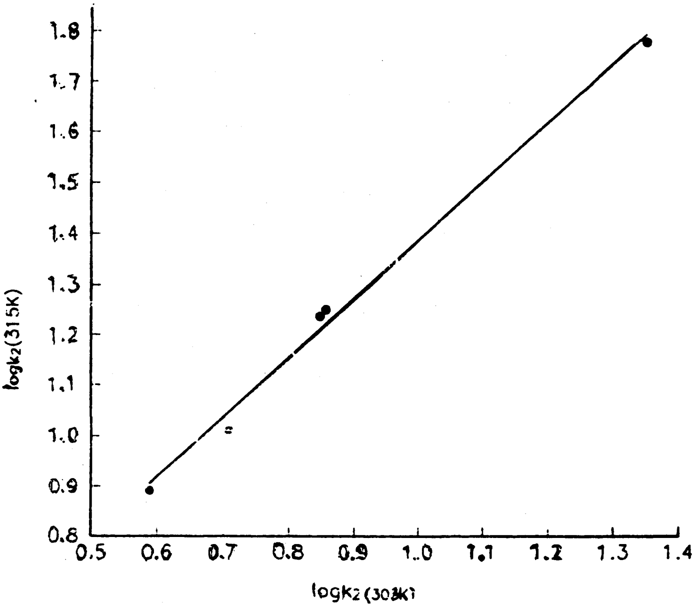


Fig. 1 Exner's plot for hypochlorite oxidation of benzaldehydes

Effect of $[H^+]$ was studied using sulphuric acid (0.002 to 0.2 mol dm^{-3}). The result showed that the rate increased with $[H^+]$ with fractional order dependence. The polarity of the medium was varied by using different percentage of acetic acid (20–60% v/v). The rate increased with decrease of dielectric constant of the medium indicating operation of a dipole-dipole interaction. Temperature coefficient of the rate of oxidation was studied by varying temperatures from 303 to 315 K. The activation parameters for various substituted benzaldehydes were calculated from the plots of log k_2 *vs.* 1/T and log k_2/T *vs.* 1/T (Table-2).

TABLE-2
ACTIVATION PARAMETERS FOR THE HYPOCHLORITE OXIDATION OF ALDEHYDES IN AQUEOUS ACETIC ACID (20%)

Substituents	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} s^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
p-$CH_3C_6H_4CHO$	44.88	42.36	151.30	89.05
C_6H_5CHO	47.02	44.45	142.28	87.56
o-ClC_6H_4CHO	64.89	62.30	82.45	87.78
p-BrC_6H_4CHO	61.13	59.55	90.05	87.35
p-ClC_6H_4CHO	65.47	63.80	76.88	87.09
p-$NO_2C_6H_4CHO$	67.45	64.87	62.77	84.24

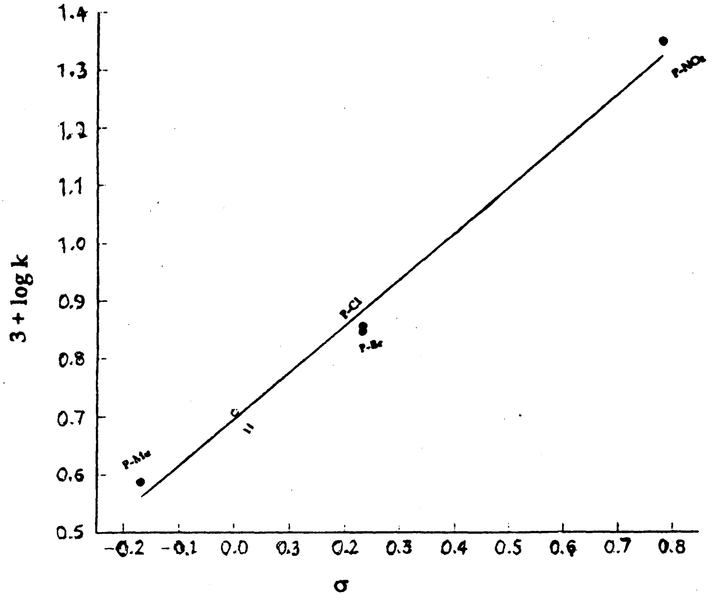
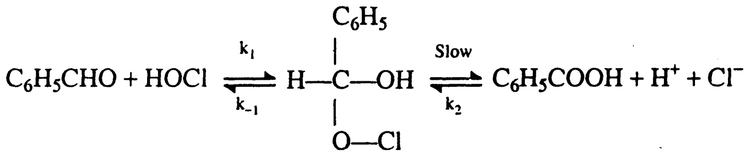


Fig. 2 Hammet plot for hypochlorite oxidation of benzaldehydes

Exner's linear isokinetic relationship[9], *viz.*, $\log k_2 = a + b \log k_1$ was tested by plotting $\log k_2$ *vs.* $\log k_1$ where k_2 and k_1 are the rate constants at the extreme temperatures T_2 and T_1 respectively (Fig. 1). The isokinetic temperature (β) calculated from the equation $\beta = T_1T_2\ (b - 1)/(T_2b - T_1)$ was 258 K. Excellent linear fit according to the Hammet relationship was found (correlation coefficient $r = 0.99$) for different substituents (Fig. 2). The large positive value of the reaction constant ($\rho = +0.80$) is in agreement with the fact that the reaction is accelerated by electron withdrawing groups.

The proposed mechanism involves the initial formation of HOCl followed by its interaction with the aldehyde forming a complex. This complex undergoes C—H bond cleavage in a slow rate determining step to form the corresponding carboxylic acid as shown.

$$OCl^- + CH_3COOH \overset{K}{\rightleftharpoons} HOCl + CH_3COO^-$$



$$C_6H_5CHO + HOCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H\text{—}\underset{\underset{O\text{—}Cl}{|}}{\overset{\overset{C_6H_5}{|}}{C}}\text{—}OH \underset{k_2}{\overset{\text{Slow}}{\rightleftharpoons}} C_6H_5COOH + H^+ + Cl^-$$

Based on the above scheme the rate of the reaction is given by

$$dx/dt = k_2[\text{complex}]$$

where $$[\text{complex}] = k_1[C_6H_5CHO][HOCl]$$

$$\therefore\ dx/dt = k_1k_2[C_6H_5CHO][HOCl]$$

The negligible salt effect observed is in conformity with the reaction between two dipolar molecules. Since the reaction involves the formation of an activated complex which is less polar than the reactants, the reaction rate increases with decrease of dielectric constant as suggested by Laidler[10]. However, the observed rate of increase with percentage of acetic acid is lower than expected. This may be due to the solvation of the reactants in aqueous acetic acid medium which decrease their energy which results in an increase of energy of activation and consequent decrease of rate[11].

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