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Kinetics and Mechanism of Oxidation of Benzaldehyde and Substituted Benzaldehyde by N-Chlorosaccharin

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The kinetic study for the rate of the oxidation of benzaldehyde and *o*-chlorobenzaldehyde with N-chlorosaccharin in aqueous acetic acid and perchloric acid medium is reported. The reaction is of first-order with respect to oxidant and substrate both. The reactions are acid catalyzed. Various thermodynamic parameters have been evaluated. The hydrated form of substrate is oxidized rapidly to corresponding acids with H_2O^+Cl species of NCSA. The possible reaction path for their formation is proposed in the light of kinetic data.

Key Words: Kinetics, Oxidation, Benzaldehyde, Substituted benzaldehyde, N-Chlorosaccharin.

INTRODUCTION

Oxidation reactions incorporating N-chlorosaccharin (NCSA) are of considerable academic and technological importance. Recently NCSA has been employed in oxidation reactions, which is obviously favourable for the extraction of electrons from an electron-rich site in a molecule.

Although the kinetics and mechanism of NCSA oxidation of organic compounds have received much attention and attracted several laboratories, most of the work in this direction was carried out using several oxidizing agents, *e.g.*, $KMnO_4^1$, Cr(IV)[2], Cr(IV)[3], V(V)[4], Tl(III)[5], CAT[6], NBA[7], NBSA[8]. However, similar studies on mechanism of oxidation of benzaldehyde and *o*-chlorobenzaldehyde with NCSA are lacking. The results of investigation on the kinetics of oxidation of benzaldehyde and *o*-chlorobenzaldehyde by N-chlorosaccharin have been reported.

EXPERIMENTAL

The reagents employed were of benzaldehyde (Merck), *o*-chlorobenzaldehyde (Riedel) grade. The solutions of N-chlorosaccharin[9] and substrates were prepared in glacial acetic acid (BDH) after weighing their appropriate quantity.

The reaction was carried out by mixing the required quantity of substrate's solution with solutions of NCSA at desired temperature maintained with an accuracy of ±0.1°C.

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The unreacted NCSA at different intervals of time was estimated iodometrically[10] against a standared solution of hypo. Several experiments were performed and always reproducible results were obtained. The corresponding aromatic acids were identified as the common product of oxidation of these systems by paper chromatography. The stoichiometric determination gave 1 : 1 mole ratio of aldehydes and NCSA.

The formation of free radical species was ruled out during the course of reaction by added acrylonitrile monomers, according to the reaction:

$$RC_6H_4CHO + C_6H_4COSO_2NCl + H_2O \rightarrow RC_6H_4COOH + HCl + C_6H_4COSO_2NH$$

where R = H for benzaldehyde and R = Cl for substituted benzaldehyde respectively.

RESULTS AND DISCUSSION

The kinetic data for oxidation of benzaldehyde and *o*-chlorobenzaldehyde with NCSA in aqueous acetic acid and in presence of $HClO_4$ acid have been obtained over a wide range of concentrations.

The nature of reaction can be shown by the plot of unreacted [NCSA] against time (Fig. 1). The pseudo first-order reaction is quite obvious from the data (Table-1), where k_1 values remain fairly constant. Similarly the oxidation rate was found directly proportional to first power of [substrate], *i.e.*, the order of reaction is unity with respect to substrate even up to five-fold variation.

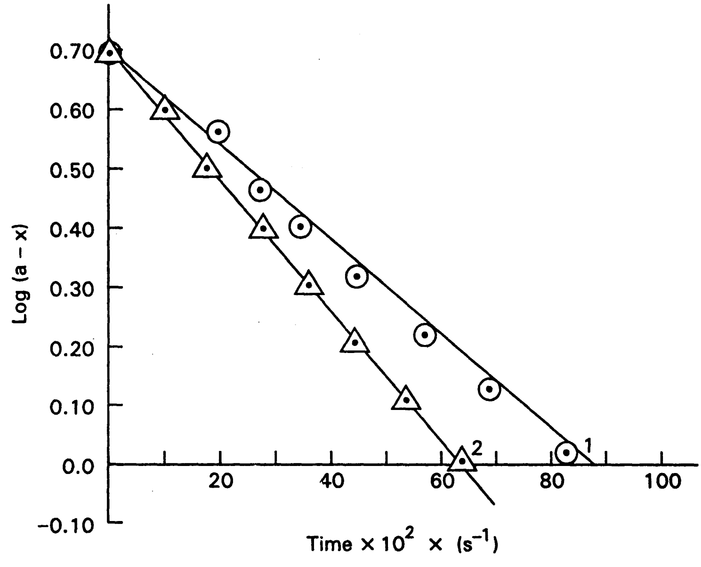


Fig. 1. Typical plot of log (a – x) versus time 1. benzaldehyde; 2. *o*-chlorobenzaldehyde [aldehyde] × 10^2 (mol dm^{-3}) = 5.0 (1.2) [$HClO_4$] (mol dm^{-3}) = 0.008(1); HOAc—H_2O (% V/V) = 20(1), 0.05 (2); 30(2); t°K = 333(1), 313(2)

TABLE-1

EFFECT OF [NCSA] ON THE RATE CONSTANT k_1

NCSA × 10^3 (mol dm^{-3})	Benzaldehyde (1) ($k_1 \times 10^4$ s^{-1})	*o*-Chlorobenzaldehyde (2) ($k_1 \times 10^4$ s^{-1})
1.00	1.914	—
1.25	—	0.711
2.00	1.981	1.123
2.50	1.931	1.395
4.00	1.950	2.149
5.00	1.846	2.523

[aldehyde] × 10^2 (mol dm^{-3}) = 5.0 (1); 1.25 (2), [$HClO_4$] × (mol dm^{-3}) = 0.008 (1), 0.05 (2),
[HOAc-H_2O % v/v] = 20 (1); 30 (2), Temperature (K) = 333 (1); 313 (2);

The plot of k_1^{-1} against $[RCHO]^{-1}$ shows no sign of complex formation (Fig. 2). The reactions are acid catalyzed.

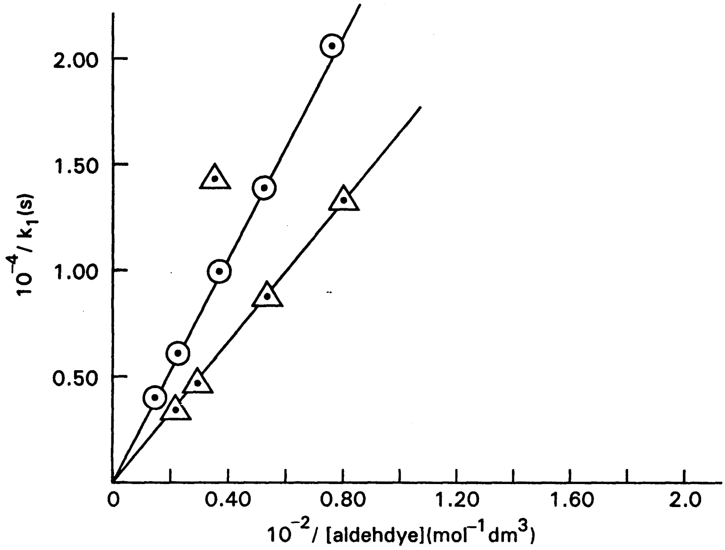


Fig. 2. [Dependence] of k_1^{-1} on $[aldehyde]^{-1}$ [NCSA] × 10^3 (mol dm^{-3}) = 5.0 (1), 1.25 (2) conditions are same as in Fig. 1

The addition of sodium perchlorate increases the rate of oxidation of the reaction slightly. The inhibition in reaction velocity was observed in the system with added saccharin.

The rate of oxidation of substrates decreases with increase in percentage composition of acetic acid (Table-2).

TABLE-2
EFFECT OF SOLVENT COMPOSITION ON THE RATE CONSTANT k_1

HOAc-H_2O (% v/v)	$10^3/D$	Benzaldehyde (1) [$k_1 \times 10^4$ (s^{-1})]	*o*-Chloro benzaldehyde (2) [$k_1 \times 10^4$ (s^{-1})]
10	15.50	2.036	—
20	17.17	1.846	2.850
30	19.15	1.583	2.662
40	21.98	1.371	2.371
50	25.64	—	2.147

[NCSA] × 10^3 (mol dm^{-3}) = 5.0 (1); 1.25 (2); other conditions are same as in Table-1.

The following probable reacting species for NCSA are proposed:

$$\text{NCSA} + H^+ \rightleftharpoons \text{NCSAH}^+ \quad (1)$$

$$\text{NCSA} + H^+ \rightleftharpoons \text{Saccharin} + Cl^+ \quad (2)$$

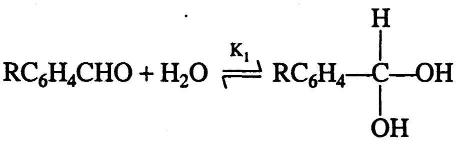
$$\text{NCSA} + H_2O \rightleftharpoons \text{HOCl} + \text{Saccharin} \quad (3)$$

$$\text{HOCl} + H^+ \rightleftharpoons H_2O^+Cl \quad (4)$$

$$\text{NCSAH}^+ + H_2O \rightleftharpoons H_2O^+Cl + \text{Saccharin} \quad (5)$$

In presence of perchloric acid, NCSA and HOCl get protonated [equations (1), (5)]. Further moreover, it has been found that H_2O^+Cl is a more powerful electrophile than Cl^+, that is why the rate of oxidation is faster in presence of $HClO_4$. Thus, the only choice was left to assume and propose the profile H_2O^+Cl as an active species of the oxidant NCSA analogous to H_2O^+Br[8]. The present study rules out the participation of enol tautomer of aldehyde.

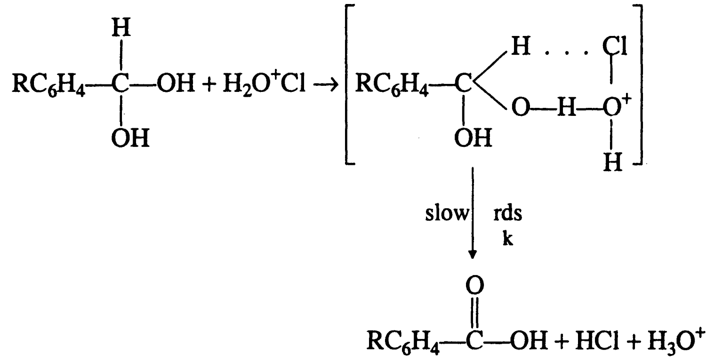
The involvement of existing hydrated aldehydes with electrophilic attack H_2O^+Cl in the rate determining step is evidenced by the medium effect studies[8, 11–13]



$$RC_6H_4CHO + H_2O \overset{K_1}{\rightleftharpoons} RC_6H_4{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}{-}OH \quad (1)$$

$$\text{NCSA} + H_2O \overset{K_2}{\rightleftharpoons} \text{Saccharin} + \text{HOCl} \quad (2)$$

$$\text{HOCl} + H^+ \overset{K_3}{\rightleftharpoons} H_2O^+Cl \quad (3)$$



(4)

where R stands for H and Cl for corresponding aldehyde. A similar type of mechanistic path has been reported in the reaction between benzaldehydes and NBSA[8, 14, 15]. The above mechanism is supported by the fact that H_2O plays an important role as it enters in the system and causes O—H bond cliff off by proton. Another feature in favour of the above cited mechanism is sufficiently high rate in lower acetic acid concentration.

Thus, considering the equilibrium condition for steps 1 and 2 and solving in terms of total NCSA concentration, the final rate law is derived in equations (5) and (6).

$$\text{Rate} = k[RC_6H_4CH(OH)_2][H_2O^+Cl] \tag{5}$$

$$k = \frac{kK_1K_2K_3[RC_6H_4CHO][H^+]}{[\text{Saccharin}] + K_2 + K_2K_3[H^+]} \tag{6}$$

at low cocentration of H^+ ions. Assuming the inequality $K_3 \ll K_2$, the equation (6) reduces to

$$k_{obs} = \frac{kK_1K_2K_3[RC_6H_4CHO][H^+]}{[\text{Saccharin}] + K_2} \tag{7}$$

The rate law equation (7) apparently accounts for the observed kinetics excellently.

The observed order of reactivity is benzaldehyde > *o*-chlorobenzaldehyde.

The above order of reactivity may be explained on the basis of variation in the rate with the introduction of substituents of different nature in benzene ring, inductive and +M effect clearly indicates that the fission of the C—H bond is faster than O—H cleavage. The negative reaction constant ρ value (–3.09) suggests an electron deficient centre.

The –I and +M effect both are dominating for chlorine atom, hence decrease in rate is observed. This is further supported by isomeric nature of the substrate and H-bonding present in the system. The oxidation of ortho-isomer of chloro benzaldehyde is faster than para-isomer; this is probably due to intermolecular hydrogen bonding with ortho-chloro isomers that facilitate stabilization of the hydrate (gem-diols) form of it in the pre-equilibrium.

The $\Delta G^{\#}$ values (90.75–97.38 kJ mol^{-1}) for the system are in close agreement with one another justifying identical mechanism operative in the system. The transition state prevents the rigid transitional and rotational freedom of the molecules that diminishes the entropy of the system.

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