

Research Articles**Oxidative Study of Substituted Benzaldehydes by N-chlorosaccharin****Gunjan Singh¹, M.N. Swami², Sweeta Neraj³, Archana Gautam⁴, Santosh K. Singh**¹Department of Chemistry, S.G.S. Govt. P.G. (Auton.) College Sidhi (M.P.) India.² Department of Chemistry, R.V.P.S. Govt. College, Umaria (M.P.) India.³Department of Chemistry, Govt. College, Maihar (M.P.) India.⁴Department of Chemistry, Govt. Girls Degree Collge, Rewa(m.p.) India⁵Department of Chemistry, Govt. T.R.S. Collge, Rewa(M.P.) India.**Received:** 27/01/2016**Revised:** 02/02/2016**Accepted:** 15/02/2016***ABSTRACT***

The oxidative kinetic studies of o- and m-nitrobenzaldehydes have been carried out by N-chlorosaccharin in 30% acetic acid-water (v/v) in presence of perchloric acid at 313 K. The reaction velocity indicated first-order dependence with respect to [oxidant], [substrate] and [H⁺]. The retarding trend in velocity of the reaction was observed with increase in dielectric constant of the medium. The added reduction product saccharin ebbs reaction rate whereas addition of NaCl and KCl slightly increase the rate of oxidation. The postulated H₂O⁺Cl reacting species of oxidant react with 1:1 mole of enolic o- and m-nitrobenzaldehydes to form corresponding nitrobenzoic acids as end-products. Various thermodynamic parameters were determined and suitable mechanism in consonance with kinetic findings was proposed.

Key Words : ebbs, consonance, postulated, retarding trends, pre-dominates.

Introduction

In the present investigation N-chlorosaccharin NCSA has been employed as an oxidant for kinetic oxidation of substrates. The acyl and sulphonyl group provide a larger orbital for electron delocalisation. It has been reported¹ that >N-Cl bond undergoes heterolytic fission in polar medium producing Cl⁺ ion, a stronger oxidant than Br⁺ ion.

The kinetic exploration of oxidation of alcohols^{2,3} hydroxy acids^{4,5} acetyl, mandelic acids⁶ benzoyl acetone⁷, and aliphatic aldehydes⁸ etc. involving N-halo-oxidant (NCSA) have been studied as reported in literature.

The studies of oxidation kinetics of ortho and meta-nitrobenzaldehydes have also been acclaimed earlier by various authors with different oxidants such as KMnO₄^{9,10}, Cr(IV) and (VI)¹¹, V(V)¹², hexacyanoferrate(III)¹³, Ir(IV)¹⁴, Tl(III)¹⁵, Ce⁺⁴ ions¹⁶ etc.

The literature survey pertaining to the oxidation kinetics of ortho- and meta-nitro- benzaldehydes by NCSA reveal no report available on the foregoing study. Hence the authors have considered it worthwhile to explore the above investigation.

Experimental

All the chemicals and reagents were employed of analytical grade. The solutions used were made by using doubly distilled water and acetic acid (BDH).

The solution of NCSA was prepared by dissolving its weighed quantity in 100% CH₃COOH (BDH) and kept in amber coloured flask wrapped around black paper to save it from the action of diffused day light which alters appreciably its concentration. The purity of reagent was checked by iodometric method.

Kinetic procedure

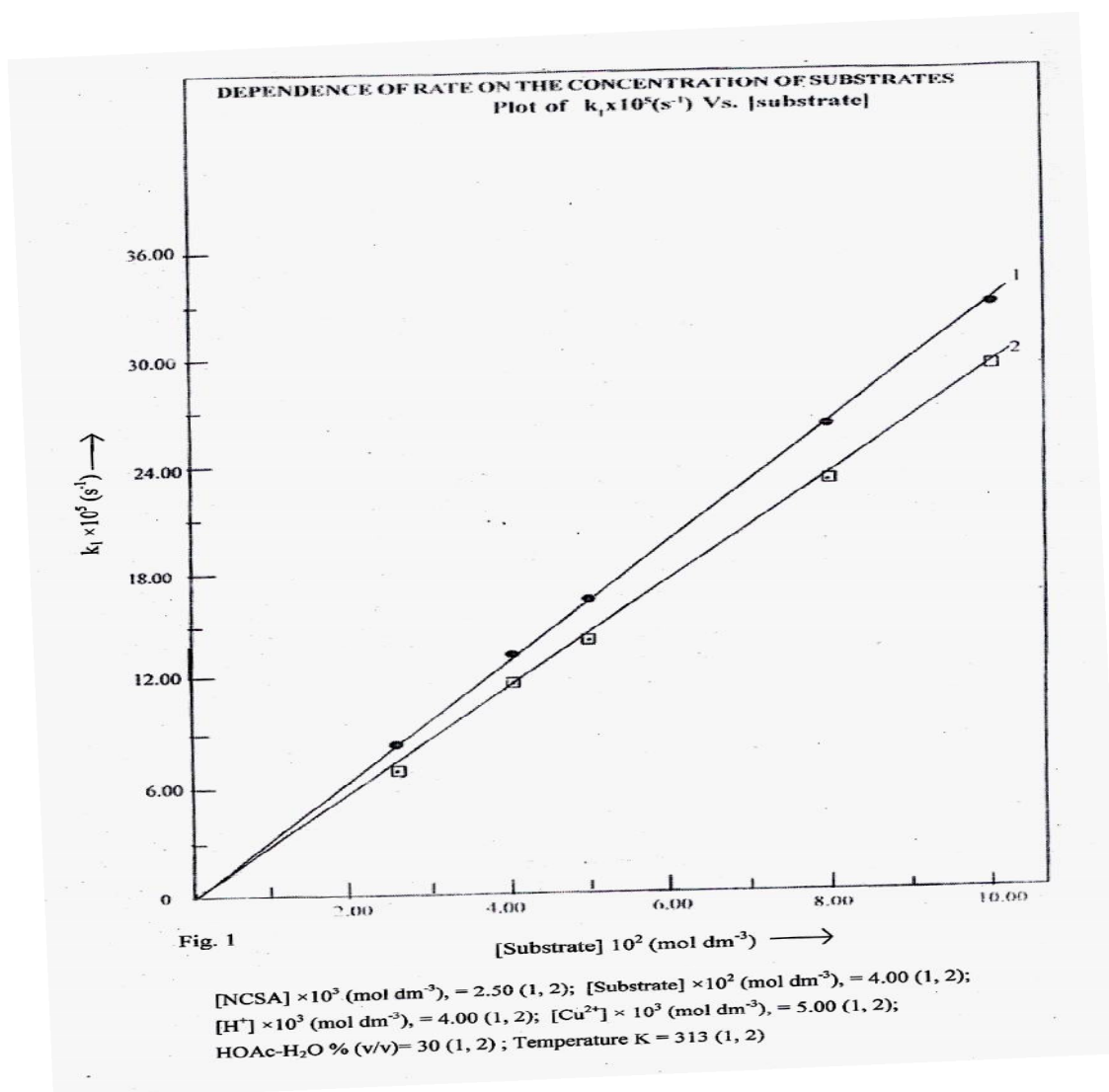
In preliminary experiments the kinetic measurements were carried out under [substrate] << [NCSA] [H⁺] pseudo first-order condition placed at experimental temperature in a thermostat maintained with a sensitivity $\pm 0.1^{\circ}\text{C}$.

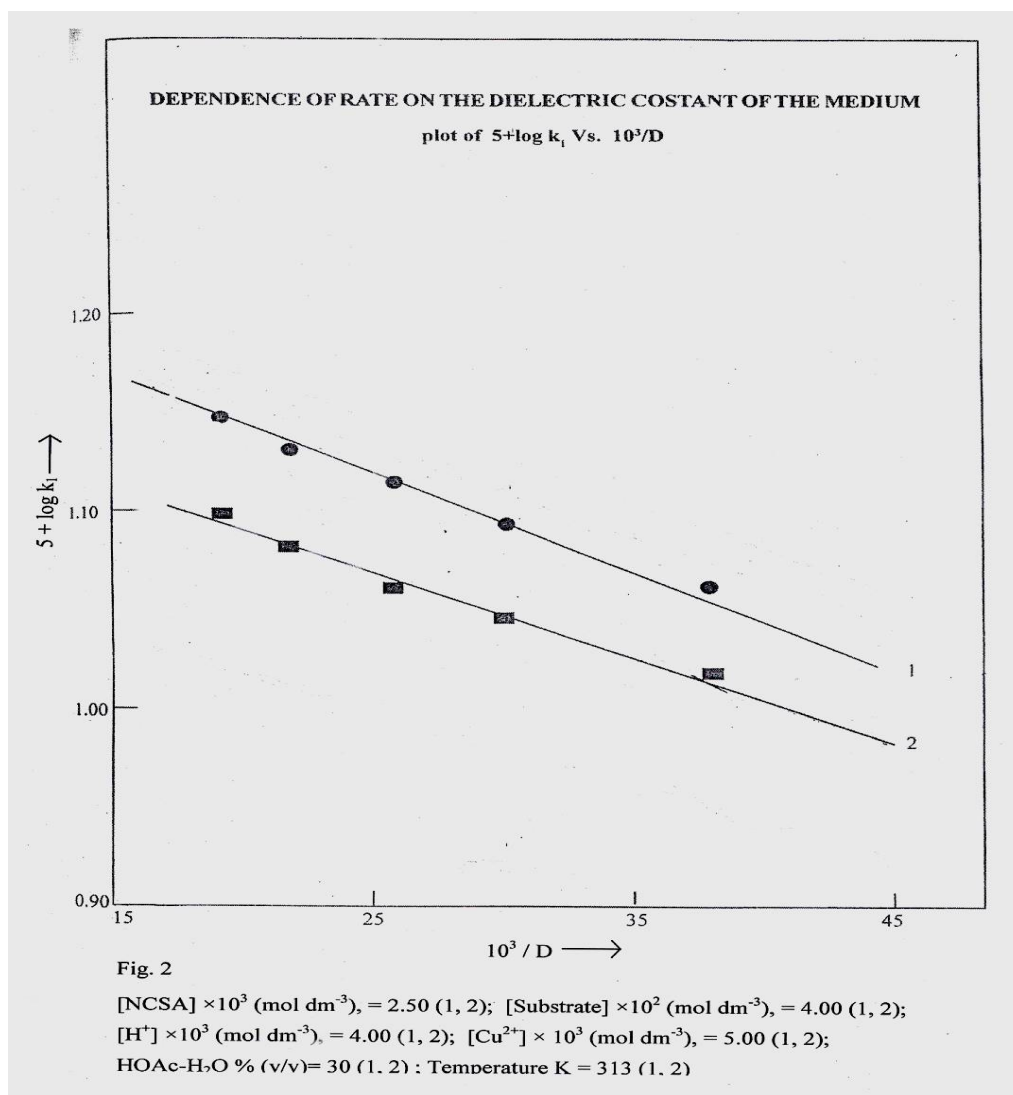
The reactions under investigation were followed by monitoring the decrease in the concentration of NCSA iodometrically for nearly 80% of the reactions. Replicate

runs indicated that velocity rate constants were reproducible within $\pm 2.0\%$. The rate constants were determined by integration, graphical and least square methods, from the liner plots of $\log a/(a-x)$ and $\log (a-x)$ versus time.

Results and Discussion

The kinetic data have been collected for five-fold $[NCSA]$ and $[substrate]$ at fixed concentration of other reactants and temperature. The studies suggested that the rate of reaction is proportional to the first power of $[oxidant]$ and $[substrate]$ (Fig. 1).





The results obtained completely rule out the formation of complex nature of the reactions. The reaction is fully catalysed by H⁺ ion. The acid catalysis may well be attributed to the protonated species of NCSA as H₂O⁺Cl. The plot of log k_{obs} versus log [H⁺] are also obtained linear with unit slope, indicating a first-order dependence on [H⁺] (Table 1). The first-order rate constant decreases with increase in solvent composition of acetic acid, plot of log k Vs. 10³/D (Fig.2). The added neutral salts like NaCl and KCl have shown insignificant effect on reaction velocity. The reaction rate slightly retards by the addition of different concentrations of reductant product saccharin. The added Cu⁺⁺ ions to reaction show acceleration in rate of oxidation while Mn⁺⁺ ions lead to retardation of the reaction rate. The estimation of unreacted NCSA showed that 1 mol of substrate reacts with 1 mol of NCSA stoichiometrically.

The corresponding substituted benzoic acids as product were analysed using existing conventional methods.

Table 1

Effect of variation of [H₂SO₄] on reaction rate

[Substrate] 10² (mol dm⁻³) = 4.0 (1,2) ; [NCSA] 10³ (mol dm⁻³) = 2.50 (1,2) ;

[Cu⁺⁺] 10³ (mol dm⁻³) = 5.0 (1,2) ; HOAc-H₂O % (v/v) = 30 (1, 2) ;

Temperature K = 313 (1, 2)

S.No.	[H ₂ SO ₄]×10 ³ (mol dm ⁻³)	← k ₁ 10 ⁵ (s ⁻¹) →	
1	2.50	8.40	7.19
2	4.00	13.50	12.04
3	5.00	16.50	15.71
4	8.00	26.20	23.97
5	10.00	32.97	29.32

1. o-nitrobenzaldehyde, 2. m-nitrobenzaldehyde

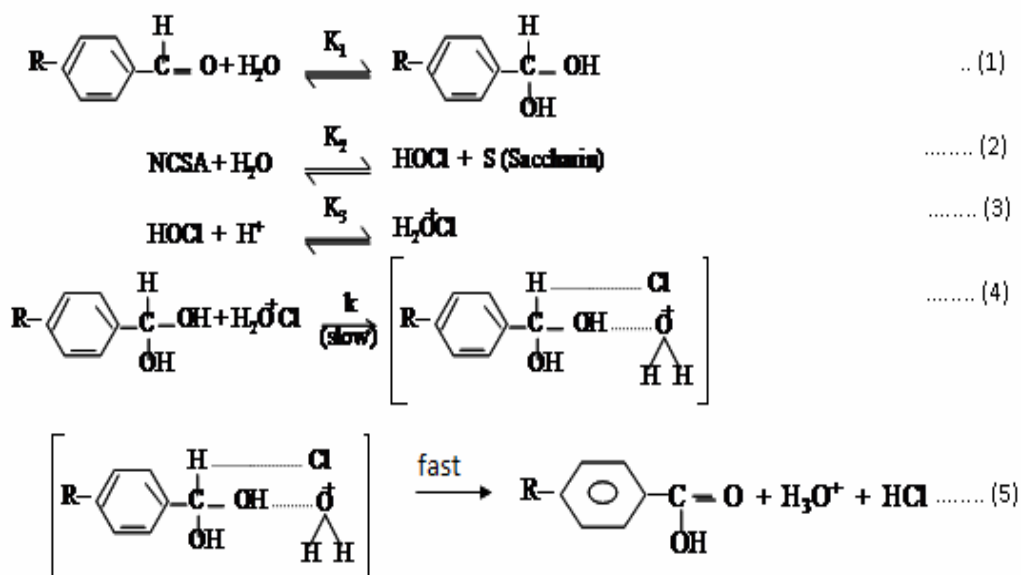
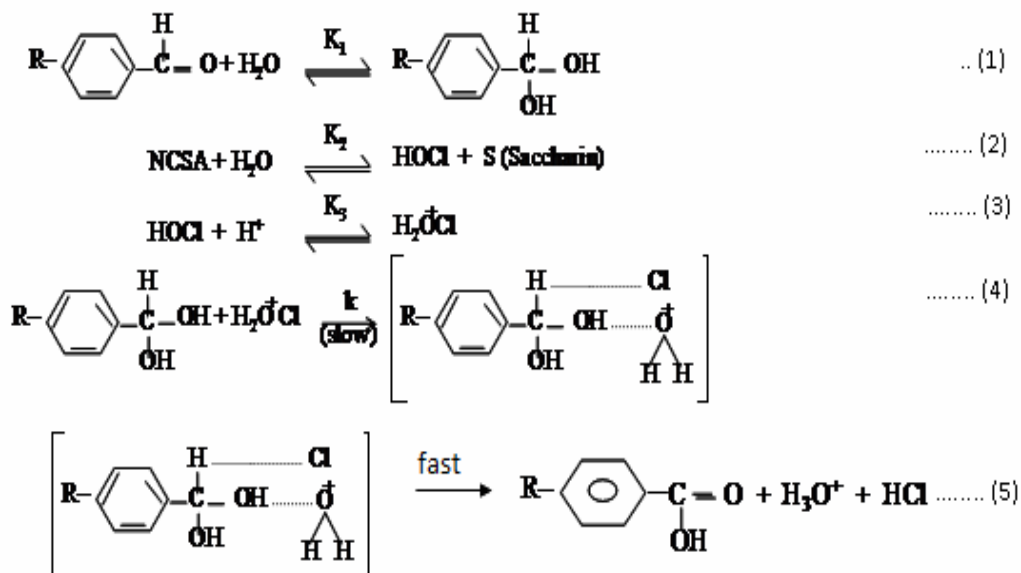
Table 2

Activation parameters for the oxidation of o-and m-nitrobenzaldehydes – NCSA system

S. No.	Substrate	E _a kJ mol ⁻¹	A (s ⁻¹)	ΔH [#] kJ mol ⁻¹	ΔG [#] kJ mol ⁻¹	-ΔS [#] Jk ⁻¹ mol ⁻¹
1.	o-nitrobenzaldehyde (o-NO ₂ C ₆ H ₄ CHO)	54.58 ±0.86	1.06×10 ⁵ ±0.01	80.18 ±0.36	91.82 ±0.85	130.44 ±0.48
2.	m-nitrobenzaldehyde (m-NO ₂ C ₆ H ₄ CHO)	55.85 ±0.38	2.20×10 ⁵ ± 0.53	82.19 ±0.58	92.13 ±0.83	132.09 ±0.50

Mechanism

Based on the kinetic observations, a suitable mechanism could be proposed as per following scheme

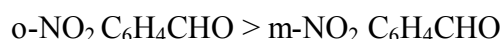


(where R = o-NO₂ and m-NO₂ groups)

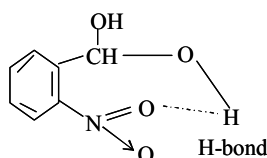
The derived rate law

$$k_{\text{obs}} = \frac{k K_1 K_2 K_3 [\text{R C}_6\text{H}_4\text{CHO}] [\text{H}^+]}{[\text{S}] + k_2} \quad \dots\dots (6)$$

Explains excellently all the experimental results accordingly. The observed reactivity for the present investigation is



which is due to showing intramolecular hydrogen bonding with o-nitro isomer that facilitate stabilization of the hydrate (gem-diols), formed in the pre equilibrium step involving C–H and O–H bond:



o-nitrobenzene hydrate
(gem- diols)

Similar trend for the order of reactivity has also been reported by several researchers when oxidation of benzaldehyde and substituted benzaldehydes was carried out with other oxidants, viz. V(V)¹², NBSA¹⁷ and NBB¹⁸.

The activation parameters are presented in Table 2. The ΔG^\ddagger value indicates that similar mechanism is operative for the oxidation of o- and m-nitro benzaldehydes – NCSA system. The values of entropy pf activation also suggest that the reaction is enthalpy controlled.

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