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Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by N-Chloronicotinamide in Aqueous Acetic Acid Medium

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The kinetics of oxidation of aromatic aldehydes by N-chloronicotinamide (NCN) have been studied in 90% acetic acid-water mixture. The reaction is first order each in [NCN] and [aldehyde] and [H^+]; with an increase in the amount of acetic acid in its aqueous mixture, the rate increases. The reaction does not induce polymerisation of acrylonitrile. Electron donating groups accelerate the rate while electron withdrawing groups decrease the rate. The reaction rates have been studied at different temperatures and the activation parameters calculated. A mechanism in accordance with kinetic data has been proposed.

Key Words: Kinetics, Mechanism, Oxidation, Aromatic aldehydes, N-Chloronicotinamide.

INTRODUCTION

Kinetics of oxidation of organic compounds have received considerable attention[1–7]. Oxidation of aromatic aldehydes by trichloro isocyaurnic acid (TCI)[8], N-bromobenzamide (NBB)[9] and N-bromosuccinimide (NBS)[10] have been studied. In the present investigation, N-chloronicotinamide (NCN)[11] (Fig. 1), a new, mild, stable and efficient oxidant has been used for the oxidation of aromatic aldehydes in aqueous acetic acid medium. NCN has been used for the oxidation study of amino acids[12].

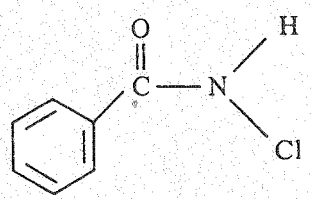

Fig. 1. N-Chloronicotinamide (NCN)

EXPERIMENTAL

NCN was prepared and purified by literature method. Acetic acid was purified by standard method and the fraction distilling at 118°C was collected. Benzaldehyde and other substituted aldehydes were the purest samples available from

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M/s Fluka Chemical Industries, Switzerland and were used as such. Analytically pure samples of sodium sulphate, nickel chloride, hydrochloric acid, nicotinamide and cyclohexene were used.

Product Analysis: Benzaldehyde (0.2 M) and NCN (0.4 M) were mixed together with 1 M HCl in 90% acetic acid (total volume 100 mL). The reaction mixture was kept aside for about 48 h for the completion of the reaction. It was then evaporated in vacuum. The residue was extracted in ether. The ether layer was separated, dried, evaporated and the residue obtained was weighed. The percentage yield was calculated to be 97%. The product was confirmed as benzoic acid by noting the mixed melting point by TLC and by spectral analysis (m.p. 121°C).

Stoichiometry: To determine stoichiometry, benzaldehyde was treated with excess of NCN. When the reaction was completed, unreacted NCN was determined iodometrically. Several determinations, using substituted benzaldehydes, indicated a 1 : 1 stoichiometry.

Kinetic Measurements: Kinetic measurements were studied under pseudo first order conditions keeping a large excess of aldehyde over NCN. The reactions were followed potentiometrically up to 70% completion by following the potentials of the reaction mixture containing varying concentrations of [NCN]/[NA] couple (NA = Nicotinamide) at regular time intervals using a platinum-saturated calomel electrode assembly. The pseudo-first order rate constant was computed from the linear plots of log ($\log E_t - E_\infty$) *vs.* time ($r > 0.99$), where E_t = potential at time 't' and E_∞ = potential at infinity (∞).

When the kinetic run was done iodometrically, the same result was obtained within ± 2%.

RESULTS AND DISCUSSION

The kinetic runs were performed in 90% acetic acid-10% water mixtures. Further, the reaction was studied in large amount of hydrochloric acid as the catalysing acid source. The oxidaion kinetics of benzaldehyde by NCN has the following salient features:

The reaction was found to be first order in [NCN] as revealed by the linear plot of log ($E_t - E_\infty$) *vs.* time ($r > 0.99$) though there was a decrease in the rate on increasing NCN concentration. The rate increases steadily with increase in [benzaldehyde]. The plot of log k_{obs} *vs.* [benzaldehyde] is linear with slope equal to unity ($r = 0.995$) indicating first order dependence on aldehyde concentration (Table-1). The second order rate constants (k_2) are found to be constant. The rate of oxidation increases linearly with the concentration of hydrocholoric acid. When the concentration of HCl is increased from 0.5–1.5 mol dm^3, the k_{obs} was found to increase from 2.05×10^{-4} to 6.08×10^{-4} S^{-1} under the condition of [NCN] = 1.0×10^{-3} mol dm^3, [benzaldehyde] = 2×10^{-2} mol dm^{-3} at 308 K and in 90% acetic acid (v/v). A plot of log k_2 *vs.* $[H^+]$ is linear with slope equal to unity ($r = 0.9985$) indicating first order dependence on $[H^+]$. The rate of oxidation increases perceptibly with increasing acetic acid content in the solvent medium.

TABLE-1

[NCN] = 1×10^{-3} mol dm^{-3}, [HCl] = 1.0 mol dm^{-3}, Solvent = 90% CH_3COOH, Temperature = 308 K

[Benzaldehyde] $\times 10^2$ mol dm^{-3}	$k_{obs} \times 10^4$ S^{-1}	$k_2 \times 10^2$ mol dm^3 S^{-1}
1.0	2.13	2.13
1.5	3.22	2.15
2.0	4.15	2.07
2.5	5.17	2.07
3.0	6.31	2.10

The rate of the reaction has not been influenced by the addition of electrolytes like sodium sulphate. Initial addition of one of the products, *viz.*, nicotinamide to the reaction mixture affects the rate. The addition of typical chlorine scavengers like nickel(II) chloride and cyclohexene does not alter the rate. Polymerization is not observed when aerylonitrile is added to the reaction mixture. Increase in temperature increases the rate of oxidation. Plots of log k_2 *vs.* 1/T are linear for all the aldehydes. Activation parameters have been calculated for all the aromatic aldehydes (Table-2) and the Exner plot is found to be linear with a correlation coefficient of 0.994. The linearity of Exner plot is suggestive of unified mechanism for the NCN oxidation of different aldehydes. From the slope of the Exner plot, the isokinetic temperature (β) was calculated as 197.24. Since it is below the experimental range (308–328), the observed effect of substituent is real.

TABLE-2
RATE CONSTANTS AND ARRHENIUS PARAMETERS FOR THE OXIDATION OF DIFFERENT ALDEHYDES

[Aldehydes] = 1×10^{-2} mol dm^{-3}, [HCl] = 1.0 mol dm^{-3}, [NCN] = 1×10^{-3} mol dm^{-3}, Solvent = 90% CH_3COOH

Y =	$k_2 \times 10^2$ mol^{-1} dm^3 S^{-1}			$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}
	308	318	328			
H	2.07	4.16	7.91	–54.16	–138.84	96.92
p-NO_2	1.08	2.03	4.21	–55.19	–142.02	98.93
p-Cl	1.53	2.82	5.01	–55.75	–135.79	97.18
p-Br	1.65	3.24	6.64	–55.86	–136.48	97.90
p-CH_3	2.48	5.03	10.12	–56.09	–133.62	97.24
p-OCH_3	2.72	5.37	10.82	–54.97	–135.06	96.57
m-NO_2	1.40	2.84	5.60	–56.11	–136.67	98.20
m-Cl	1.73	3.49	6.63	–53.89	–142.31	97.72
m-Br	1.87	3.70	7.69	–56.17	–134.15	97.49
m-CH_3	2.28	4.64	9.09	–56.03	–133.05	97.00
m-OCH_3	2.36	4.68	9.41	–55.77	–133.57	96.91
o-NO_2	1.86	3.80	7.74	–57.29	–130.58	97.51

The oxidation of substituted benzaldehydes by NCN had been investigated under comparable conditions. All the substrates obey the same rate law as the parent substrate. Electron donating groups increase the rate while electron withdrawing groups decrease the rate of oxidation.

The order of reactivity of different aldehydes with NCN is

$$p\text{-}OCH_3 > p\text{-}CH_3 > m\text{-}OCH_3 > m\text{-}CH_3 > H > m\text{-}Br > o\text{-}NO_2$$
$$> m\text{-}Cl > p\text{-}Br > p\text{-}Cl > m\text{-}NO_2 > p\text{-}NO_2$$

The stoichiometric study shows that one mole of aldehyde consumes one mole of NCN.

$$X—Ar—CHO + NCN + H_2O \longrightarrow X—Ar—COOH + NA + HCl$$

The Exner plot is linear with correlation coefficient 0.9944.

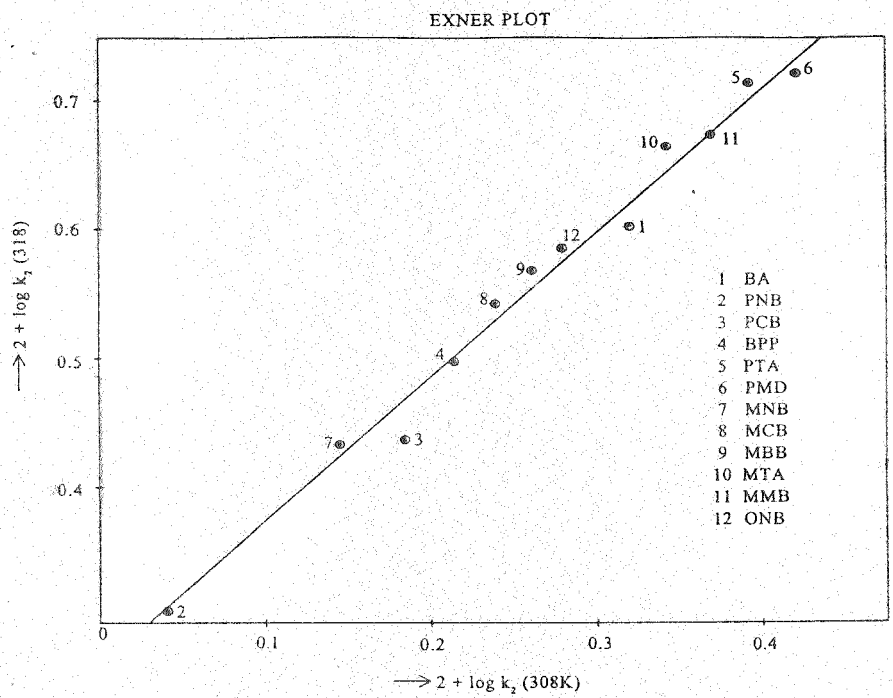


Fig. 2. Plot of log k_2 (308) *vs.* log k_2 (318)

Hence any mechanism proposed for the oxidation of aromatic aldehydes by NCN should be capable of accounting the above observations. Further the active oxidising species has to be identified before any mechanistic interpretation could be advanced.

Under the experimental conditions studied, the following five oxidising species, *viz.*, Cl_2, HOCl, H_2OCl^+, $NCNH^+$ and NCN in aqueous solutions are important. The oxidation of amino acids by NCB[13] and CBT[14] had been reported to take place through the intermediate formation of protonated oxidant or molecular chlorine. Similar arguments may be extended to oxidation of aromatic aldehydes by NCN since NCN also belongs to the same class of N-haloamides.

It has been reported that the oxidation of amino acids with NCN under similar conditions proceeds through the formation of chlorine[12].

Molecular chlorine may not be the oxidising species since the rate is not influenced by the initially added nickel(II) chloride and cyclohexene which are well known chlorine scavengers.

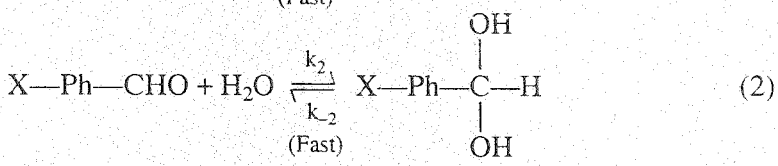
In the proposed cyclic mechanism the involvement of either NCN as such or HOCl as the active oxidising species will lead to a rate law which will not explain the dependence of the rate of oxidation on HCl concentration. Also the sensitivity of the rate on the polarity of the solvent medium cannot be explained if HOCl and NCN are the oxidising species.

If $NCNH^+$ is the active oxidant, the reaction must show hydrogen ion dependence for the rate which is true in this case. But $NCNH^+$ cannot form a cyclic transition state necessarily needed for explaining the experimental results and substituent effects.

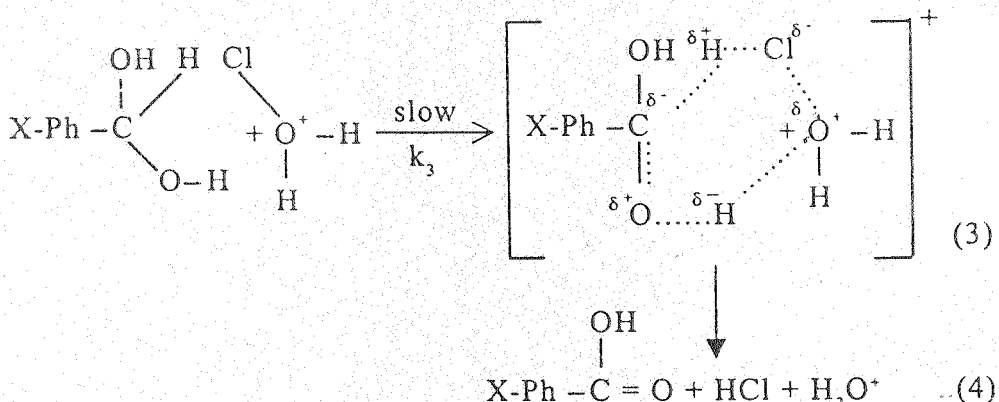
Hence hydrated chloronium ion, *i.e.*, H_2OCl^+ may be the most probable oxidising species. This can fit into all the experimental results in the oxidation of aromatic aldehydes.

Therefore the following scheme of mechanism is proposed for the present oxidation study.

$$NCN + H_2O + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NA + H_2OCl^+ \quad \text{(Fast)} \qquad (1)$$



(Fast) (2)



(3)

(4)

Hydrated chloronium ion is formed in the first step by the acidic hydrolysis of NCN. This may act as the active oxidant attacking the hydrated aldehyde molecule formed as indicated in eqn. (2).

The reaction is retarded by the addition of nicotinamide. This suggests that the pre-equilibrium step involves a process in which nicotinamide is one of the products. No chlorine is formed in this mechanism which rules out the oxidation by molecular chlorine. Step (1) of this explains the first order dependence on HCl concentration.

This mechanism suggests a six-membered cyclic transition state with a positive charge distributed over a large space in the complex. It fairly accounts for the experimental results. The rate determining step (3) involves a reaction between an ion and a dipole, *i.e.*, hydrated aldehyde and H_2OCl^+ which accounts for the negligible electrolyte effect in the reaction.

The transition state is less polar than the reactants. This may be responsible for the increase in the rate with increased percentage of acetic acid.

It was estimated that the 'ρ' value of this reaction as –0.402. Negative ρ value points out that the intermediate involved may be a positively charged species. Small magnitude of ρ may be indicative of cyclic electron transfer in the transition state. Electron withdrawing groups such as *p*-NO_2 should retard the rate while electron donating groups such as *p*-OCH_3 should accelerate the rate. This is observed in the experiments. Smaller magnitude of the ρ value may be indicative of limited influence of the substituents present in the aldehyde moiety of the transition state during the reaction. It is to be emphasised that the substituents exert their electronic influence on the structure and stability of the activated complex thereby giving rise to different reaction rates.

The proposed rate equation is

$$\text{Rate} = \frac{k_3K_1K_2[\text{Aldehyde}][\text{NCN}][H^+]}{[\text{NA}]} \quad (5)$$

The experimental kinetic data collected lead to the following rate law:

$$\text{Rate} = k_{obs}[\text{Aldehyde}][\text{NCN}][H^+] \quad (6)$$

where $k_{obs} = \frac{k_3K_1K_2}{[\text{NA}]}$, $K_1 = \frac{k_1}{k_{-1}}$ and $K_2 = \frac{k_2}{k_{-2}}$.

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