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Chlorination of Phenol and *p*-Nitrophenol by N-Chloronicotinamide in Aqueous Acetic Acid Medium-A Kinetic and Mechanistic Study

V. PRIYA* and N. MATHIYALAGAN†
Department of Chemistry, Holy Cross College (Autonomous), Tiruchirappalli-620 002, India
E-mail: priya_733@rediffmail.com

Kinetics of chlorination of phenol and *p*-nitrophenol by N-chloronicotinamide (NCN) in the presence of $HClO_4$ in aqueous acetic acid medium have been reported. The observed rate of oxidation is first order with respect to [N-chloronicotinamide] and [H^+]. The order with respect to [substrate] is fractional. The rate of the reaction decreases with increase in the dielectric constant of the medium. The major product of chlorination of phenol and *p*-nitrophenol are 4-chlorophenol and 2-chloro 4-nitrophenol, respectively. Arrhenius and activation parameters have been calculated. A suitable mechanism has been proposed and a rate law explaining the experimental results is derived.

Key Words: Kinetics, Chlorination, N-Chloronicotinamide and Phenols.

INTRODUCTION

The chlorination of phenols by N-chlorosuccinimide[1], sodium hypochlorite in aqueous alkaline medium[2] and bromination of phenol and substituted phenols by N-bromosuccinimide[3] have been reported earlier. Chlorination of anisole and *p*-nitroanisole by N-chlorosuccinimide[4] and iodination of phenols by N-iodosuccinimide[5] have also been reported. This prompted us to undertake the present studies on chlorination of phenol and *p*-nitrophenol by N-chloronicotinamide. N-Chloronicotinamide (NCN) is a new, mild, stable, efficient and inexpensive oxidant[6] for organic substrates. The compound has been established as an effective source of positive halogen. The kinetics of oxidation of amino acids[7], aldehydes[8], alcohols[9], primary alcohols[10] and benzyl ethers[11] by N-chloronicotinamide have been reported.

EXPERIMENTAL

Commercial sample of phenol was purified before use. *p*-Nitro phenol was used as such. N-Chloronicotinamide was prepared by the chlorination of nicotinamide. Standard solution of N-chloronicotinamide was prepared in water and strength was checked by iodometric method. Acetic acid (AnalaR, Qualigen) was purified by standard method[12]. Perchloric acid and sodium sulphate used were of AnalaR grade.

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†Department of Chemistry, St. Joseph's College (Autonomous), Tiruchirappalli-620 002, India.

Kinetic measurements: All solutions were thermostated for 0.5 h before mixing. The kinetic runs were carried out under pseudo first order condition ([substrate] > [N-chloronicotinamide]). Rate studies were carried out at a constant temperature. Requisite amount of substrate in aqueous acetic acid, perchloric acid and sodium sulphate were taken in the reaction vessel and placed in a water thermostat maintained at 328 K. Reaction was initiated by the rapid addition of N-chloronicotinamide solution and its progress was followed by estimating iodometrically the amount of unconsumed N-chloronicotinamide at regular intervals of time.

Stoichiometry and product analysis: The stoichiometry of the reaction was determined by taking excess of N-chloronicotinamide over the substrate and allowing the reaction for completion. Estimation of unreacted N-chloronicotinamide showed that one mole of substrate consumed one mole of N-chloronicotinamide. For product study, the substrate was taken in excess compared to that of oxidant concentration. Reaction mixture was kept in hot water bath for *ca.* 4 h. After that it was cooled and poured into a separating funnel. Solvent ether was added and shaken well. Then it was washed with distilled water. The ether layer was collected and dried with anhydrous sodium sulphate. The product was confirmed to be chlorinated derivatives by spot test and by direct comparison with authentic samples.

RESULTS AND DISCUSSION

The kinetics of chlorination of phenol and *p*-nitro phenol by N-chloronicotinamide has been investigated at several initial concentrations of the oxidant. The pseudo first order rate constant remains constant with the increase in the initial concentration of the oxidant (Table-1). In each kinetic run the reaction shows no deviation from the first order plot of log [N-chloronicotinamide] *versus* time. Hence it must be stressed that the reaction follows first order kinetics with respect to oxidant at every one of these concentrations.

TABLE-1
EFFECT OF CONCENTRATION OF N-CHLORONICOTINAMIDE (NCN) AND SUBSTRATE ON THE REACTION RATE AT 328 K
$[HClO_4] = 0.1$ M, $[Na_2SO_4] = 0.1$ M, Solvent = 80 % CH_3COOH (v/v)

[NCN] × 10^3 (M)	[Substrate] × 10^2 (M)	$k_{obs} \times 10^5$ (s^{-1})	
		Phenol	*p*-Nitro phenol
4.0	2.0	5.45	2.01
4.0	3.0	6.98	2.65
4.0	4.0	8.11	3.43
4.0	5.0	9.71	4.01
5.0	4.0	8.91	3.18
6.0	4.0	8.02	3.69
7.0	4.0	8.43	3.31

The rate of chlorination has been studied by varying the initial concentrations of substrate (Table-1). It is found that the reaction follows fractional order kinetics with respect to [substrate]. The rate of the reaction increases slightly with the increase in the concentration of the substrate. The slope of the plot of log k_{obs} *versus* log [substrate] is less than unity (0.6).

The rate of chlorination of phenols by N-chloronicotinamide decreases with the increase in the dielectric constant of the medium. Table-2 shows the variation of rate constants with the dielectric constant of the medium. An increase in the rate constant is noticed on decreasing the dielectric constant of the medium, indicating the formation of less polar activated complex than the reactant molecule[7,9,13]. Plot of log k_{obs} *versus* 1/D is found to be linear. The enhancement of the reaction rate with an increase in the amount of acetic acid may generally be attributed to two factors, *viz.*, (i) increase in acidity at constant [$HClO_4$] (ii) decrease in dielectric constant with increase in acetic acid content. The linear plots of log k_{obs} against the inverse of dielectric constant indicates the interaction between positive ion and a dipole molecule.

TABLE-2
EFFECT OF DIELECTRIC CONSTANT ON THE REACTION RATE AT 328 K
[Substrate] = 4×10^{-2} M, [NCN] = 4×10^{-3} M, [$HClO_4$] = 0.1 M, [Na_2SO_4] = 0.1 M

CH_3COOH-H_2O % (v/v)	D*	$k_{obs} \times 10^5$ (s^{-1})	
		Phenol	*p*-Nitro phenol
80-20	20.00	8.11	3.43
70-30	27.50	5.12	2.19
60-40	31.50	4.36	1.86
50-50	37.50	3.32	1.47

*D: Dielectric constant.

Effect of [H^+] is investigated by varying [$HClO_4$] at constant [substrate] and [N-chloronicotinamide]. There is a significant increase in the rate of chlorination with the increase in [$HClO_4$] as shown in Table-3. The plot of log k_{obs} *versus* log [$HClO_4$] is linear with unit slope.

TABLE-3
EFFECT OF CONCENTRATION OF PERCHLORIC ACID ON THE REACTION RATE AT 328 K
[Substrate] = 4×10^{-2} M, [NCN] = 4×10^{-3} M,
[Na_2SO_4] = 0.1 M, solvent = 80 % CH_3COOH (v/v)

[$HClO_4$] (M)	$k_{obs} \times 10^5$ (s^{-1})	
	Phenol	*p*-Nitro phenol
0.1	8.11	3.43
0.2	16.22	7.16
0.3	24.49	10.22
0.4	32.36	13.86

The chlorination of phenol and *p*-nitro phenol by N-chloronicotinamide is studied at different temperatures (323-338 K). The rate of chlorination increases with the increase in the temperature (Table-4). Arrhenius plot of log k_{obs} *versus* 1/T is linear.

The energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), entropy of activation ($\Delta S^{\#}$) and pre-exponential factor A are calculated (Table-5).

TABLE-4
EFFECT OF TEMPERATURE ON REACTION RATE
[Substrate] = 4×10^{-2} M, [NCN] = 4×10^{-3} M, [$HClO_4$] = 0.1 M,
[Na_2SO_4] = 0.1 M, solvent = 80 % CH_3COOH (v/v)

Temperature (K)	$k_{obs} \times 10^5$ (s^{-1})	
	Phenol	*p*-Nitro phenol
323	6.65	2.03
328	8.11	3.43
333	9.55	4.88
338	10.94	6.29

TABLE-5
ACTIVATION PARAMETERS FOR THE CHLORINATION OF PHENOLS AT 323 K

Substrate	Ea (kj mol^{-1})	log A	$\Delta H^{\#}$	$\Delta G^{\#}$	$\Delta S^{\#}$
Phenol	31.26	6.848	28.54	62.30	-102.93
p-Nitro phenol	70.68	0.877	67.96	101.71	-53.86

Mechanism: N-Chloronicotinamide (NCN) is a source of positive halogen and the reagent has been exploited as oxidant for a variety of substrates. The nature of active oxidizing species and the mechanism depend on the nature of the halogen atom, the groups attached to the nitrogen and the reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. The probable reactive species of N-chloronicotinamide in acid solution are HOCl, $NCNH^+$, H_2OCl^+ and N-chloronicotinamide itself in aqueous solution. A simultaneous attack of H^+ and Cl^- ion on the N-haloamide can lead to the release of molecular chlorine, as in the case of oxidation of amino acids[7] by N-chloronicotinamide. HOCl acts as the effective oxidizing species in the oxidation of aliphatic alcohols by N-chloronicotinamide[9].

The chlorination of anisole and *p*-nitroanisole[4] is reported to take place through the protonated form of N-chlorosuccinimide. The oxidation of aromatic aldehydes by NCS[14] also take place through $NCSH^+$. The oxidation of amino acids by N-chlorobenzamide[15] and chlorobenzotriazole[16] has been reported to take place through the intermediate forms of protonated species of the oxidant or molecular chlorine. The oxidation of alcohols and aliphatic ketones by N-chlorosuccinimide[17] and N-bromosuccinimide[18] take place through the protonated species $NCSH^+$ and $NBSH^+$. In the present study of chlorination of phenols by N-chloronicotinamide, the rate of the reaction increases with the increase in the [acid]. Hence the reaction is said to be catalyzed by H^+ ions. Taking into account of all the kinetic observation and the above fact in view, it is assumed that $NCNH^+$ is the effective oxidizing species in the present investigation.

Based on the above observation, the following mechanism has been proposed for the N-chloronicotinamide chlorination of phenols.

$$\text{NCN} + \text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NCNH}^+ \qquad (1)$$

$$\text{NCN}^+ + \text{X-C}_6\text{H}_4\text{OH} \xrightarrow[\text{slow}]{k_2} \text{Product} \qquad (2)$$

$X = H, NO_2$

Applying steady state approximation to $NCNH^+$, the following rate law is suggested.

$$\text{Rate} = \frac{k_1k_2[\text{NCN}][\text{H}^+][\text{X}-\text{C}_6\text{H}_4\text{OH}]}{k_{-1} + k_2[\text{X}-\text{C}_6\text{H}_4\text{OH}]}$$

The rate law accounts for the fractional order dependence on [substrate], first order dependence on [NCN] and [$HClO_4$]. The proposed mechanism is well supported by the moderate value of energy of activation and thermodynamic parameters (Table-5). The order of the reactivity is phenol > *p*-nitrophenol. It is seen from Table-5 that the activation energy is highest for the slowest reaction.

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