

Research Articles

STUDY ON KINETICS AND MECHANISM OF OXIDATION OF 2-PHENYLETHYLAMINE BY N-CHLOROPHTHALIMIDE IN PRESENCE OF HYDROCHLORIC ACID IN METHANOL- WATER MEDIUM

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ABSTRACT:

A kinetic study of oxidation of 2-phenylethylamine (2-PEA), a bioactive compound, with potent oxidant, N-Chlorophthalimide (NCP) has been carried out in the presence of HCl in methanol-water medium, at 308 K. The experimental rate laws obtained are: $-d [NCP]/dt = k [NCP][2-PEA][H^+]$ in methanol-water medium. The reaction is fully acid catalyzed and retardation of the added phthalimide. Variation of ionic strength of the medium shows negligible effect on rate of reaction. Decrease in dielectric permittivity of the medium decreased the rate. The stoichiometry of the reaction was found to be 1:1. The oxidation products of 2-PEA were identified as the 2-phenylacetaldehyde. The reactions were studied at different temperatures and the activation parameters have been evaluated. The reaction constants involved in the proposed mechanisms were computed. The proposed mechanisms and the derived rate laws are consistent with the observed experimental results.

Keywords: Kinetics, N-Chlorophthalimide (NCP), 2-phenylethylamine, 2-phenylacetaldehyde, eco-friendly

INTRODUCTION

Chemistry is often cited as a style of chemical synthesis that is consistent with the goals of green chemistry. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice. It is distinct from environmental chemistry, which focuses on chemical phenomena in the environment. Environmental concern has forced the chemical industry to re-evaluate many of its processes to reduce or eliminate the formation of waste produced in the synthesis of organic products. This need is specially required in oxidation technology and can be addressed by the development of clean and safe oxidation Procedures. This is possible by establishment of green catalytic process by use of environmentally friendly oxidant or green catalysts.

In present paper we explored the kinetics of oxidation of 2-phenylethylamine (PEA) with oxidant, Chlorophthalimide (NCP) because it is an eco friendly, cheap, easily synthesized in chemical laboratories, available in the market. 2-Phenylethylamine (PEA) is a naturally occurring endogenous amine, which is present in several mammalian tissues¹ including the brain¹. 2-Phenylethylamine is formed by decarboxylation of amino acid, L-phenylalanine². It crosses the presynaptic membrane and potentiates the postsynaptic effects of dopamine³. 2-PEA may act as neuromodulator of catecholamine neurotransmission in the brain³. This bioactive amine is also present in certain foodstuffs such as chocolate, cheese and wine and may cause undesirable side effects in susceptible individuals⁴. After reviewing the literature we found that there was only information available on the oxidation kinetics

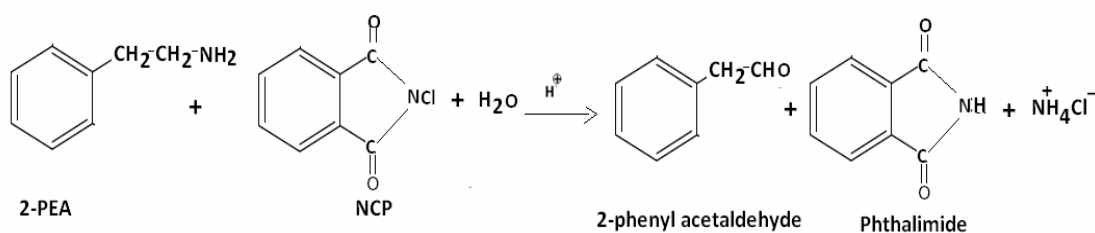
of 2-phenylethylamine with N-Chlorophthalimide⁵. N-Chlorophthalimide is a source of positive halogen, and this reagent has been selectively used as an oxidant for a variety of substrates in both acid and alkaline media⁶. This potent oxidizing agent has been used in the oxidation of primary alcohols⁷, methyl sulphide⁸. In the present work, the kinetics of oxidation of 2-PEA with NCP in acid has been studied with a view to elucidate the mechanism of the reaction and to identify the reactive species of oxidant in methanol-water medium.

MATERIALS AND METHODS

The oxidant N-Chlorophthalimide (Aldrich sample), 2-phenylethylamine (sigma chemicals) were used and purified by the literature procedure⁹. The standard solution of 2-phenylethylamine (sigma chemicals sample) was prepared in acetic acid. Double distilled water employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of N-Chlorophthalimide was stored in an amber colored bottle and its strength was checked iodometrically⁹ using 1 % solution of freshly prepared starch as an indicator.

Kinetic measurements: All kinetic measurements made under pseudo first-order conditions, by keeping large excess of 2-phenylethylamine over oxidant N-Chlorophthalimide. Mixture containing requisite amount of solutions of N-Chlorophthalimide, and HCl in 30 % acetic acid equilibrated at 308 K. To this mixture added a measured amount of pre-equilibrated at 308 K., standard solution of N-Chlorophthalimide. To maintain the desired temperature (within $\pm 0.1^\circ\text{C}$) the reaction mixture was kept in a thermo stated water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals.

Stoichiometry and Product Analysis: Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of N-Chlorophthalimide over 2-phenylethylamine and hydrochloric acid in 30 % Me,OH for 24 hrs. at 308 K. The un-reacted oxidant (N-Chlorophthalimide) was determined by iodometrically. The estimated amount of un-reacted N-Chlorophthalimide showed that one mole of 2-phenylethylamine consumes one mole of 2-phenylethylamine. The 2-phenylethylamine found as the end-product of oxidation. These products were identified by forming their 2,4-dinitrophenylhydrazone (2-phenyl acetaldehyde 2,4-DNP, M.P. 121⁰C), Which were characterized by their melting point.



RESULTS AND DISCUSSION

The oxidation of 2-PEA with NCP was kinetically investigated at several initial concentrations of the reactants in acid media. The salient feature obtained is discussed. Under pseudo-first-order conditions ($[2\text{-PEA}] \gg [\text{NCP}]$) at constant $[\text{HCl}]$, solvent composition and temperature, plots of $\log(a-x)$ vs. time were linear ($r > 0.994$) indicating a first-order dependence of rate on $[\text{NCP}]$. The pseudo-first-order rate constants (k_1) calculated is given in Table 1.

Further, the values of k_1 calculated from these plots are unaltered with variation of [NCP], confirming the first-order dependence on [NCP]. The rate constant (k_1) have been found to increase with increase in the concentration of 2-phenylethylamine and plot of k_1 Vs [2-phenylethylamine] was linear with slope less than unity, indicating a fractional order dependence on rate of 2-phenylethylamine (Fig.1,2, Table-1).

Table- 1: Effect of variation of reactants on pseudo first-order rate constant k_1 at 308K.

10^2 [2-PEA] (mol. dm. ⁻³)	10^3 [NCP] (mol. dm. ⁻³)	10^3 [H ⁺] (mol. dm. ⁻³)	% Me.OH-H ₂ O (v/v)	$k_1 \times 10^4$ (s ⁻¹)
1.25	1.00	1.25	30	1.30
1.25	1.25	1.25	30	1.29
1.25	2.00	1.25	30	1.28
1.25	2.50	1.25	30	1.29
1.25	4.00	1.25	30	1.31
1.25	5.00	1.25	30	1.24
1.00	2.50	1.25	30	1.03
1.25	2.50	1.25	30	1.29
2.00	2.50	1.25	30	1.69
2.50	2.50	1.25	30	1.91
4.00	2.50	1.25	30	2.31
5.00	2.50	1.25	30	2.40
1.25	2.50	1.00	30	0.87
1.25	2.50	1.25	30	1.29
1.25	2.50	2.00	30	2.25
1.25	2.50	2.50	30	2.88
1.25	2.50	4.00	30	4.83
1.25	2.50	5.00	30	5.75
1.25	2.50	1.25	20	0.87
1.25	2.50	1.25	30	1.18
1.25	2.50	1.25	40	1.29
1.25	2.50	1.25	50	1.42
1.25	2.50	1.25	60	1.67

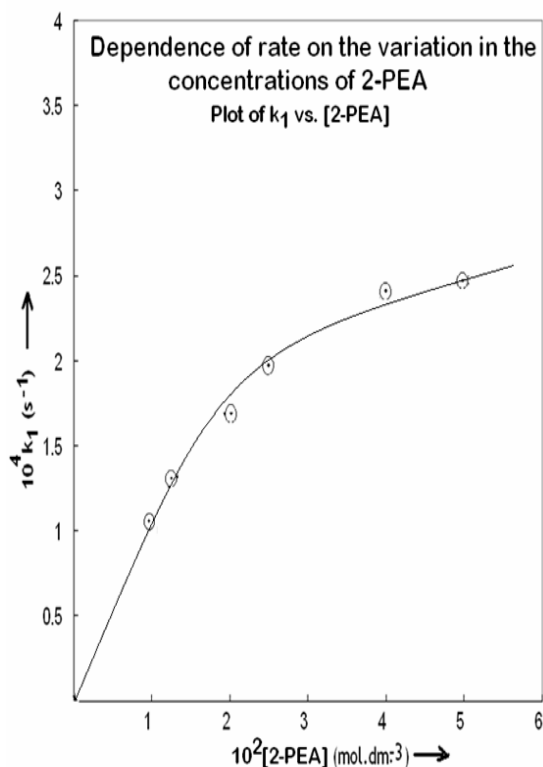


Fig.1: Effect of variation in the concentration of 2-PEA

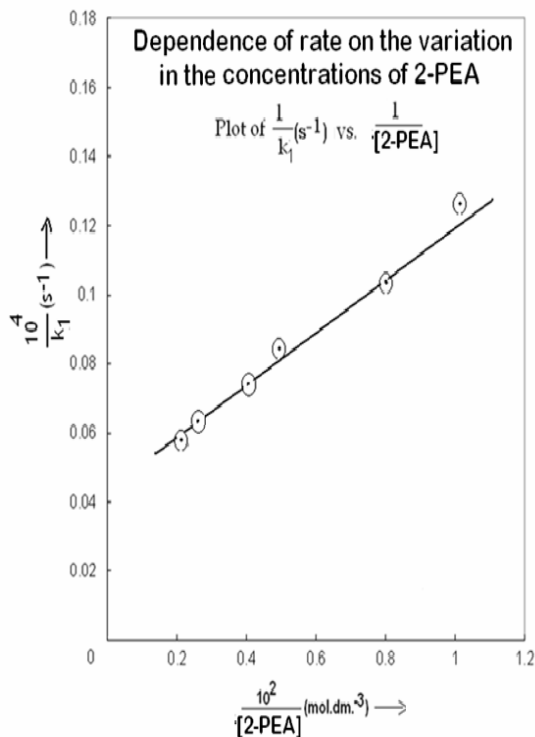


Fig.2: Effect of variation in the concentration of 2-PEA

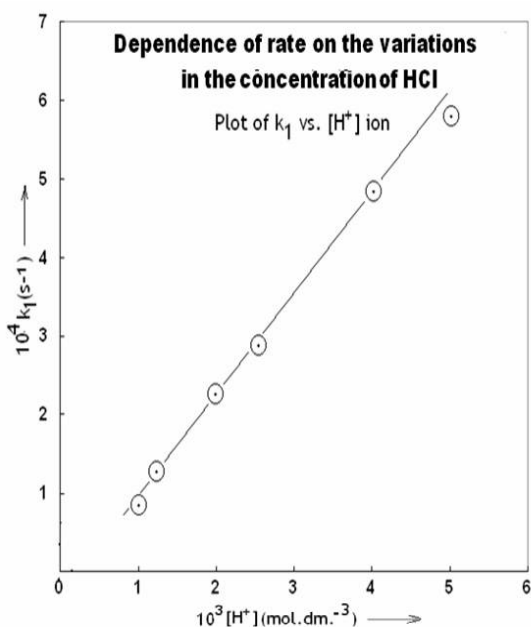


Fig.3: Effect of variation in the concentration of HClO₄

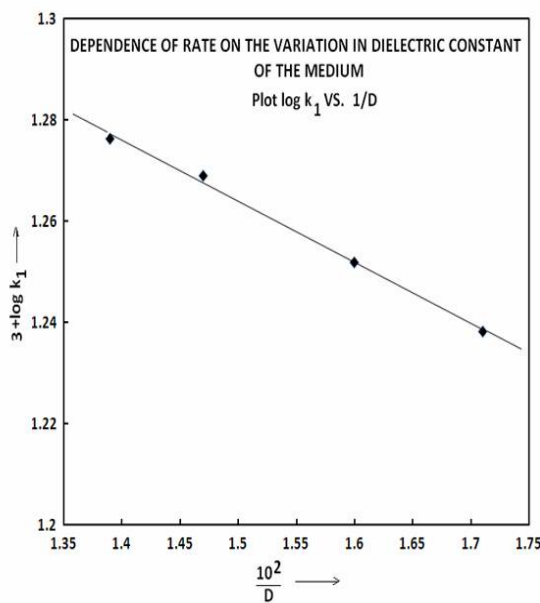


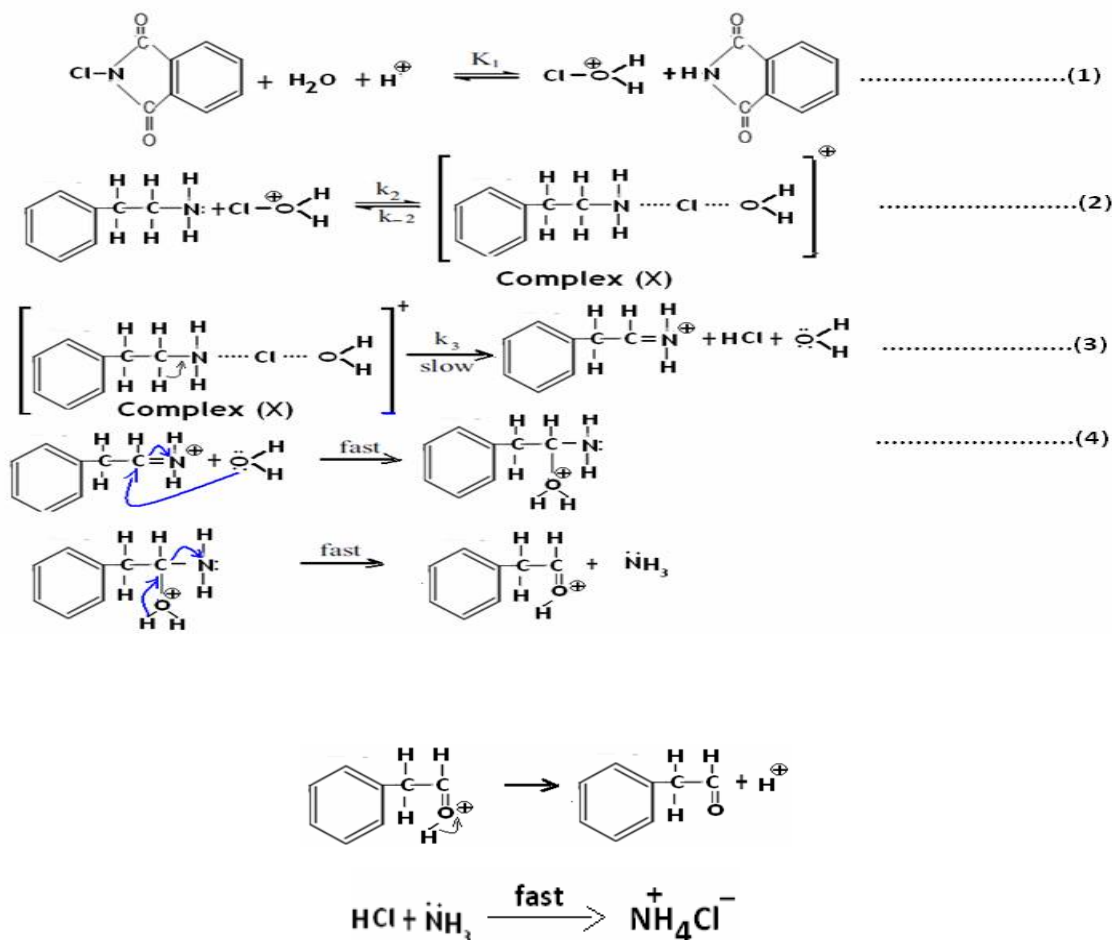
Fig.4: Effect of variation in the dielectric constant of the medium

Similarly, the reaction is fully acid catalyzed because, the rate of reaction increases with increase in [HCl] (fig.3, Table: 1).The effect of changing solvent composition on

the reaction rate was studied by varying concentration of Me.OH from 20-60 %. The rate constants suggest that the rate of reaction slightly decreases with increasing Me.OH content of the solvent mixture. The plot of $\log k_1$ Vs $1/D$ was found to be linear with negative slope indicating the involvement of two dipoles or an ion-dipole reaction (fig.4). Variation of phthalimide one of the products of oxidation, had negative effect on the rate of reaction. The HCl catalyzed oxidation reaction of 2-phenylethylamine with NCP at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate, which may be attributed to the inertness shown by free radicals.

Reactive Species and Mechanism: It has been shown that probable reactive species of NCP in acid solution are NCP itself or Cl^+ or protonated NCP viz., $NCPH^+$ or (H_2O^+Cl) as active oxidizing species, and negative effect of the initially added product, phthalimide restricts us to take H_2O^+Cl as the oxidizing species. Based on the above discussions and observed kinetic data, a probable mechanism is proposed for the oxidation of 2-PEA.

MECHANISTIC PATHS FOR THE OXIDATION 2-PHENYLETHYLAMINE



In above Scheme, S is the substrate; X is a substrate-reactive species complex.

The derived rate equation is:

$$k_{obs.} = \frac{K_1 k_2 k_3 [H^+] [2 - PEA]}{[NHP] \{k_{-2} + k_3\}} \dots \dots \dots (5)$$

Effect of temperature: The rate of oxidation was determined at different temperatures and the Arrhenius plots of $\log k$ vs. $1/T$ were all linear from this plot, the activation and thermodynamic Parameter for equilibrium step and rate determining step of the scheme was evaluated (Table 2).

Table: 2

Thermodynamic Parameter

<i>Substrate</i>	<i>E_a</i> (kJ mol ⁻¹)	<i>A</i> (s ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger JK mol ⁻¹
2-PEA	50.94 ±0.16	3.34 x10 ³ ±0.77	49.45 ±0.47	-78.91 ±0.23	-90.39 ±0.19

The observed ΔS^\ddagger values are large and negative. It may be interpreted that the fraction of collisions become more stringent and decomposition of activation complex is a quite slow process. ΔH^\ddagger indicates that the reactions are enthalpy controlled. Further, the constancy in the calculated values of ΔG^\ddagger for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction.

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