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KINETIC STUDY OF OXIDATIVE DEGRADATION OF 4-OXO-4-PHENYLBUTANOIC ACID BY N-CHLOROPHTHALIMIDE IN AQUEOUS ACETIC ACID MEDIUM

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ABSTRACT:

The oxidation of 4-oxo-4-phenylbutanoic acid by a mild and selective oxidizing agent N-chlorophthalimide (NCP) leads to the formation of corresponding ketone. The reaction found first order in NCP. The reaction follows Arrhenius relationship with respect to 4-oxo-4-phenylbutanoic acid. A retarding effect of acetic acid is observed. Various thermodynamic parameters have been computed. No evidence of Polymerization of acrylonitrile showed no effect of free radical on the rate of reaction. Stoichiometric study revealed 1:1 mole ratio. On the basis of thermodynamic parameters and stoichiometry a feasible mechanism has been proposed and rate law has been derived.

Keywords: Kinetics, 4-oxo-4-phenylbutanoic acid, Mechanism, NCP, Oxidation.

INTRODUCTION

N-chlorophthalimide (NCP) is a new member of the N-halo family. NCP, the derivative of Phthalimide is a mild, stable, efficient, and inexpensive oxidant for organic substates. The elemental analysis and physical properties of NCP affirm the presence of the N-X bond. For this reason, it is possible that the compound serving as an effective source of halonium ion. The study of various compounds [1-10] reveals the mildness and selectiveness of NCP.

The oxidation kinetics of oxoacids have been extensively studied. They have substaintially helped to our understanding of mechanistic pathway for reaction.

oxoacids are studied with various oxidants and follows first order kinetics [11-21]. 4-oxo-4-phenylbutanoic acid is a oxyacid also studied individual with various oxidants [22-23].

The general review of the literature explored that no works have been reported about the oxidation of4-oxo-4-phenylbutanoic acid with NCP; so, this prompted for the present investigation and evaluate kinetic parameters as well as correlation analysis.

1. MATERIALS AND METHODS

1.1. Chemicals

Chemicals employed in this study were of A.R. grade. Double distilled water used throughout the study. The solutions were prepared without any further purification of chemicals. The solution of NCP prepared by reported method.

1.2. Kinetic experiment

The experiments were performed under pseudo-first-order conditions by keeping an excess of the substrate over NCP. The experiments were carried out in a black-coated stopper glass vessel to avoid any photochemical effect. A thermo-stated water bath maintained the desired temperature within ± 0.1K (308K). Requisite volumes of all reagents, except NCP, were introduced into a reaction vessel and equilibrated at 308K. A measured volume of NCP, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. The progress of the reactions was monitored by examining aliquots of the reaction mixture for unconsumed NCP iodometrically using starch as the indicator.

1.3. Product analysis

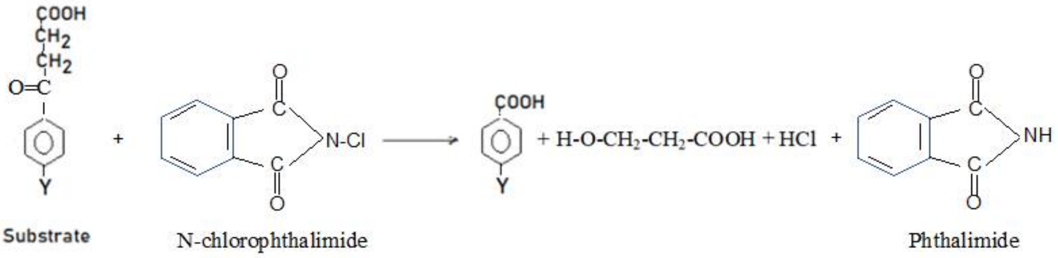
The end product from the oxidation of 4-oxo-4-phenylbutanoic acid was Benzoic Acid and its presence confirm by existing conventional methods. The analysis of end product was carried out under kinetic conditions i.e., with the excess of 4-oxo-4-phenylbutanoic acid was taken over NCP. After completion of reaction the solution is treated with an excess (200ml) of saturated solution of 2,4- dinitrophenylhydrazine (DNPH) in 2 mol/dm^3 HCl and kept in refrigerator for 24 hours. The precipitate of 2,4- dinitrophenylhydrazone (DNP) filtered, dried and weighed respectively. recrystallize the crystal of DNP with ethanol and weighed again. The DNP was found identical (m.p. and mixed m.p.) with DNP of 4-oxo-4-phenylbutanoic acid.

2. RESULT AND DISCUSSION

The oxidation of 4-oxo-4-phenylbutanoic acid was carried out by NCP at 308K under pseudo first order condition. The rate of 4-oxo-4-phenylbutanoic acid and other experimental data were obtained. Oxidation of 4-oxo-4-phenylbutanoic acid by NCP under the condition [NCP] << [4-oxo-4-phenylbutanoic acid] had the following kinetic feature.

2.1. Stoichiometric studies

The stoichiometric studies of oxidation of 4-oxo-4-phenylbutanoic acid by NCP were carried out with excess of oxidant (NCP) and maintaining other parameters constant (HOAc-H_2O = 30 % (v/v), Temperature = 308K). The stoichiometric results indicated 1 mole of substrate consumes 1 mole oxidant as represented by the following empirical equation:



Where Y= H for 4-oxo-4-phenylbutanoic acid.

There is first order rate constant is unchanged with an increase in the NCP.

2.1.1. Order with respect to [oxidant] [substrate]

When the substrate (S1) are in large excess, the plots of log (a-x) vs time **(Figure 1)** are found to be linear, indicating first-order dependence on NCP. The pseudo first-order rate constants in NCP calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration. The plot of k_1 *vs* [substrate] is initially linear passing through origin and tends to obtain limiting value, bending towards horizontal axis **(Figure 2).** Hence the reaction follows fractional order behaviour with respect to the substrate concentration.

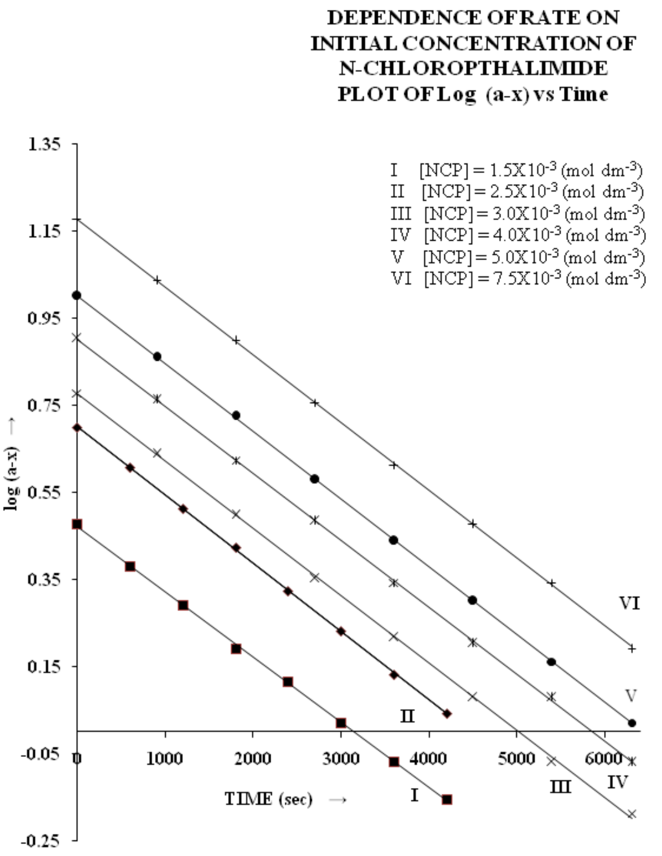


Fig. III - B1 [S1] =5.0 X 10^{-2} (mol dm^{-3}), [H^+] = 0.20 X 10^{-3} (mol dm^{-3}), HOAc - H_2O = 30% (V/V), TEMP. = 308 K.

Figure 1: The plot of log (a-x) versus time. Conditions are given in Table 1.

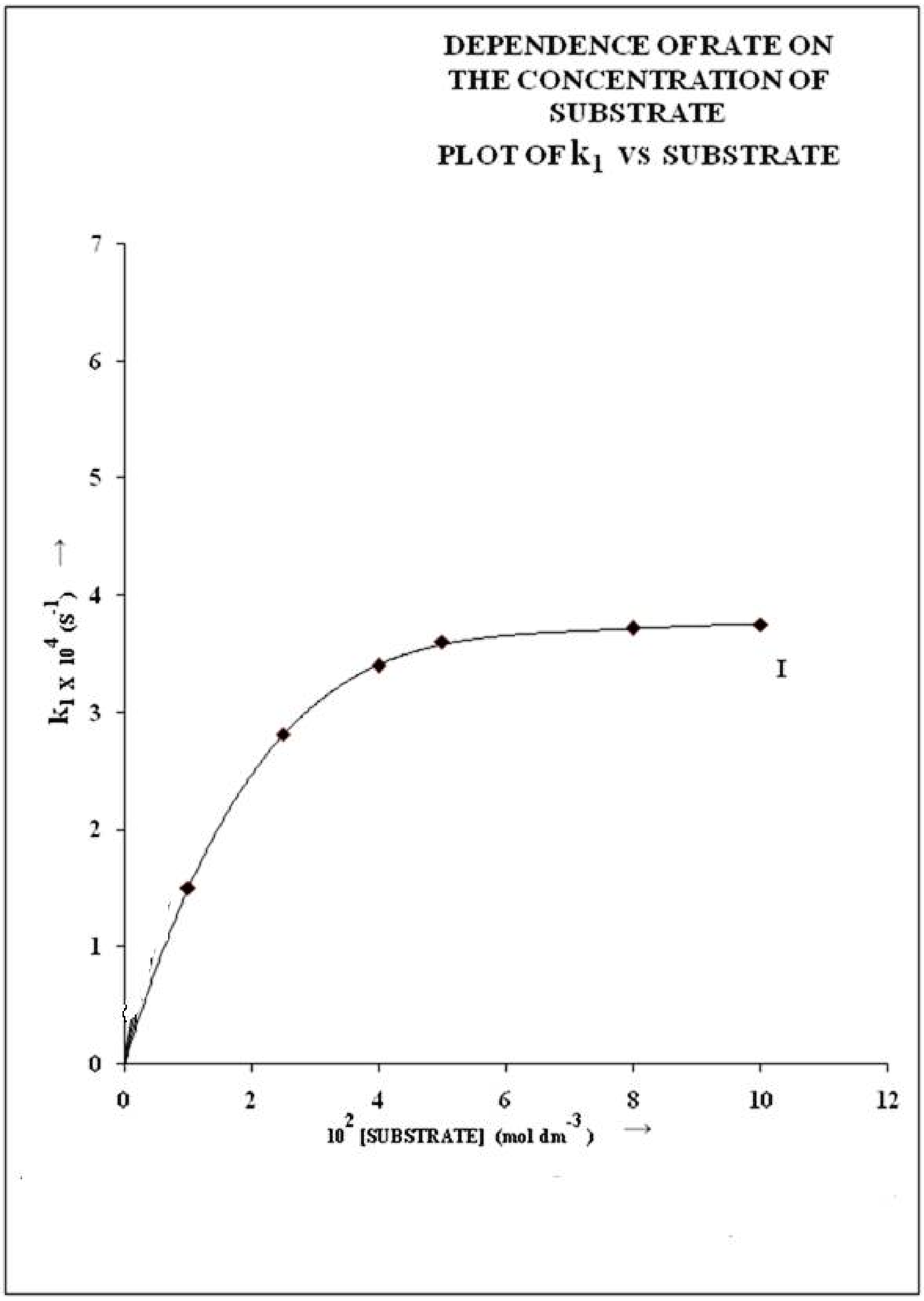


Figure 2: Dependence of k_1 on [Substrate]. Conditions are given in Table

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

10^2 [Substrate] (mol dm^{-3})	10^3 [NCP] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	% HOAc - H_2O	$k_1 x 10^3$ (s^{-1})
1.00	2.50	-	30	1.917
2.50	2.50	-	30	3.405
4.00	2.50	-	30	4.115
5.00	2.50	-	30	4.284
8.00	2.50	-	30	4.402
10.00	2.50	-	30	4.451
5.00	1.50	-	30	4.288
5.00	2.50	-	30	4.284
5.00	3.00	-	30	4.263
5.00	4.00	-	30	4.256
5.00	5.00	-	30	4.282
5.00	7.50	-	30	4.287
5.00	2.50	0.10	30	3.404
5.00	2.50	0.15	30	3.917
5.00	2.50	0.20	30	4.284
5.00	2.50	0.25	30	4.586
5.00	2.50	0.30	30	5.062
5.00	2.50	0.40	30	5.704
5.00	2.50	0.50	30	6.446
5.00	2.50	-	10	3.703
5.00	2.50	-	20	4.051
5.00	2.50	-	30	4.284
5.00	2.50	-	40	4.604
5.00	2.50	-	50	5.185

2.1.2. Effect of variation of $[H^+]$:

The catalysed kinetics was observed by the addition of perchloric acid. On varying perchloric acid concentration there is an increase in reaction rate (**Table 1**). The plot of log k_1 versus $[H^+]$ (**Figure 3**) gave a straight line with positive intercept, suggesting that acid plays a complex role in the reaction system.

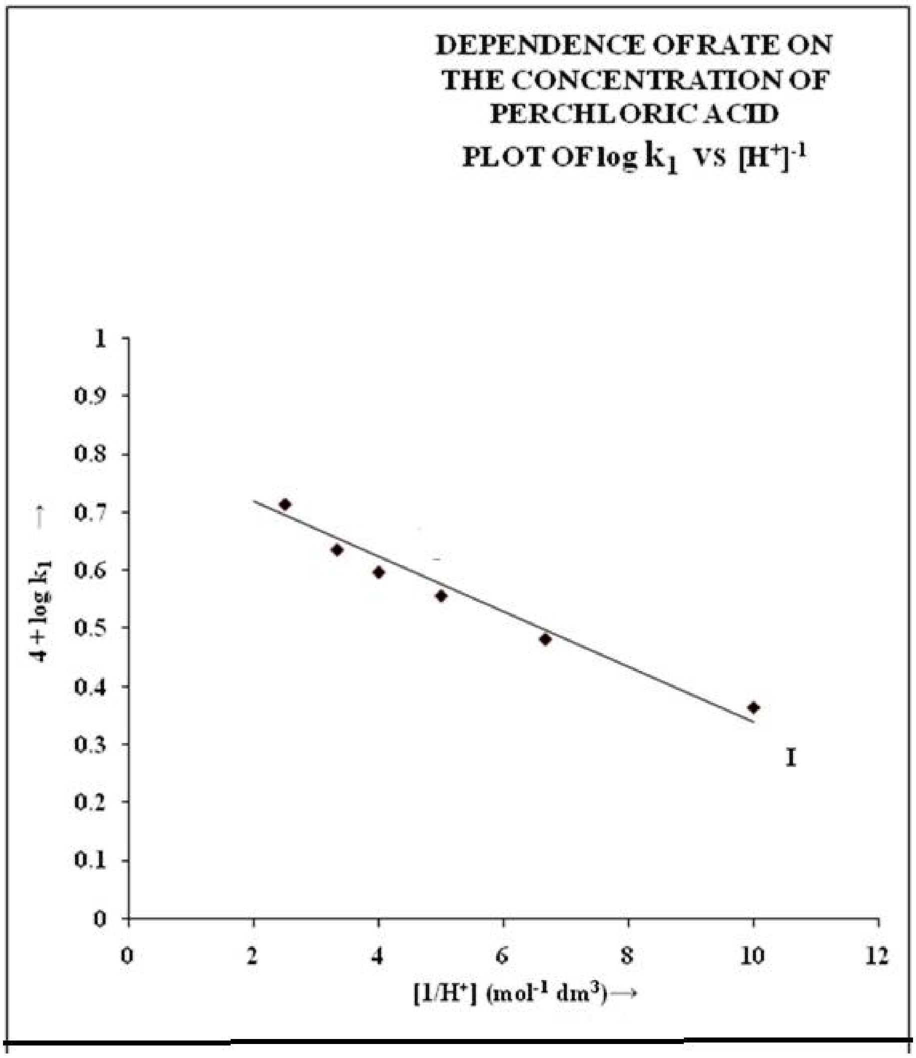


Figure 3: Dependence of k_1 on $[H^+]$. Conditions are given in Table 1.

2.1.3. Effect of solvent on reaction velocity:

The rate was studied at different concentrations of the solvent. It is observed that the rate decreases with increasing concentration of acetic acid.

2.1.4. Effect of ionic strength and Phthalimide:

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behaviour on slow step in the reaction mechanism is ruled out. Addition of phthalimide (one of the reaction products), at constant NCP and substrate concentration, decreases the rate of reaction. The retardation of reaction rate on the addition of phthalimide suggests a pre-equilibrium step that involves a process in which phthalimide is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of phthalimide concentration.

2.1.5. Effect of Product and Free Radical Inhibitor:

The reaction under study failed to induce polymerization of added acrylonitrile discarding the presence of free radicals and free radical path.

2.1.6. Effect of temperature:

The effect of temperature on the reactions of 4-oxo-4-phenylbutanoic acid with NCP in was also studied. The value of energy of activation, ΔS, ΔH & ΔG were computed. These values are summarized in **Table 2** along with the other parameters.

Table 2: Thermodynamic parameters 4-oxo-4-phenylbutanoic acid -NCP system

Substrate	Ea ($kJ\ mol^{-1}$)	A (s^{-1})	ΔH* ($kJ\ mol^{-1}$)	ΔG* ($kJ\ mol^{-1}$)	-ΔS* ($JK^{-1}\ mol^{-1}$)
4-oxo-4-phenylbutanoic acid	62.91	$1.14x10^8$	60.35	86.142	70.74

3. MECHANISM

The concentration of NCP was found to be constant over a period of time. So, it was found that there was no appreciable reaction between acid and NCP.

Retarding effect of phthalimide & solvent and positive effect of H+ clearly ruled out the NCP, CH3COOCl, CH3COO+HOCl are not prime reactive species from the list of possible reactive species. Thus, the only choice and possibility that is left as a remote prime active species more probable is for HOCl. Our kinetic finding also suggests to us to assume that HOCl is to be considered as the most predominant, fertile reacting species. This leads to the postulation of the following overall mechanism and rate law.

$$\text{NCP} + H_2O \rightleftharpoons \text{HOCl} + \text{Phthalimide}$$

$$\mathrm{NCP + H_2O \overset{K_1}{\rightleftharpoons} HOCl + Phthalimide\,(Phth)} \qquad (1)$$

$$\mathrm{HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl} \qquad (2)$$

$$\mathrm{NCP + H^+ \rightleftharpoons NCPH^+} \qquad (3)$$

$$\mathrm{NCPH^+ + H_2O \rightleftharpoons H_2O^+Cl + Phthalimide\,(Phth)} \qquad (4)$$

$$\mathrm{SA + HOCl \overset{K_3}{\rightleftharpoons} \underset{X_1^{\#}}{Complex} + H_2O} \qquad (5)$$

$$\mathrm{SA + H_2O^+Cl \overset{K_4}{\rightleftharpoons} \underset{X_2^{\#}}{Complex} + H_2O} \qquad (6)$$

$$(X_1^{\#}) \xrightarrow{k_1} \text{Products} \qquad (7)$$

$$(X_2^{\#}) \xrightarrow{k_2} \text{Products} \qquad (8)$$

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law is derived as;

$$k_{obs} = \frac{K_1\ [SA]\ (k_1 K_3 + k_2 K_4 K_2 [H^+])}{[Phth] + K_1 + K_1 K3\ [SA]} \qquad (17)$$

This proposed rate law explained all experimental facts.

4. CONCLUSION

4-oxo-4-phenylbutanoic acid is an oxo-acids. At first substrate formed a complex which is attacked by HOCl, an active species of NCP. Just like the oxidation of some other compounds with N-halo oxidants [24-26], NCP also exhibits similar kinetics with aliphatic hydroxy acid. An intermediate complex formed which is decomposes in a slow rate determining step and give the product. The reaction obeys Arrhenius relationship. The proposed mechanism is in good accordance with experimental findings.

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