# Kinetic Study of oxidation of p- chlorophenylacetic acid by N-chlorobenzimidazole

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## ABSTRACT

The kinetics of p-chlorophenylacetic acid oxidation with N-chlororobenzimidazole (NCBI) in aqueous acetic acid 30% (v/v) solution in the presence of hydrochloric acid were studied. The reaction is first order in terms of oxidant and has a Michaelis-Menten dependency on substrate concentration. The rate of reaction increases as the concentration of hydrochloric acid increased, and the order with regard to $[H^+]$ was discovered to be one. Positive solvent effect with 1:1 stoichiometry has been also observed. The activation parameters have been estimated using the kinetic data, and a reasonable mechanism has been provided.

**Key Words**: p-chlorophenyl acetic acid, kinetics, N-chlorobenzimidazole, oxidation, benzimidazole

## INTRODUCTION

The N-halo family now includes a new member, N-chlorobenzimidazole (NCBI). Benzimidazole's derivative, NCBI, is an effective, affordable, mild, stable oxidant for organic substrates[1,2]. The physical characteristics of NCBI and elemental analysis confirm the existence of the N-X bond. It is therefore plausible that the combination functions as a useful source of halonium ions. The mildness and selectivity of NCBI are demonstrated by research on leucine[3], glycine[4], furfural[5], benzyl alcohol[6], vanillin[7] and cyclanols[8].

p-chlorophenyl acetic acid, or p-Cl PAA  is a derivative of acetic acid in which one methyl hydrogen is replaced by 4-chlorophenyl group. Numerous academic researchers have documented the critical function that p-Cl PAA plays a vital role in the treatment of cancer[9] and tumor[10].

It was discovered during a general study of the literature that no studies have been reported on the oxidation of p-chlorophenyl acetic acid with NCBI; this led the current inquiry and evaluation of kinetic parameters as well as correlation analysis.

## MATERIALS AND METHODS

### Chemicals

The chemicals used in this investigation were A.R. grade. During the investigation, double-distilled water was used. No additional chemical purification was necessary during the preparation of the solutions. The NCBI solution made using the approach described.

### Kinetic demonstration

The experiment was run with an excess of substrate over NCBI, resulting in pseudo-first-order conditions. The studies were conducted in a glass stopper jar painted in black to prevent any photochemical effects. The necessary temperature was maintained within ±0.1K (308K) using a thermo-stated water bath. All reagents, with the exception of NCBI, were added in the correct amount to a reaction vessel and allowed to equilibrate at 308K. The reaction vessel was quickly filled with a measured volume of NCBI that had been separately equilibrated at the same temperature. By looking at reaction aliquots, the reactions progress was tracked.

### Product analysis

The final end product of p-chloro PAA oxidation was p-chlorobenzaldehyde, whose existence was confirmed by currently used conventional techniques. The analysis of the final result was performed under kinetic circumstances, meaning that p-chloro PAA was used in excess of NCBI. Following the conclusion of the reaction, 200 millilitres of an excess saturated solution of 2,4-dinitrophenylhydrazine (DNPH) in 2 mol/dm$^3$ HCl is added to the solution, and it is then refrigerated for a full day. The 2,4-dinitrophenylhydrazone (DNP) precipitate was filtered, dried and weighed accordingly. Use ethanol to re-crystallize the DNP crystal, and then weigh it once again. The DNP and DNP of p-chloro PAA were found to be identical (m.p. $269.5^0$C).

## RESULT AND DISCUSSION

The oxidation of p-Cl PAA was carried out by NCBI at 308K under pseudo first order condition. The rate of oxidation of p-Cl PAA and other experimental data were obtained. Oxidation of p-Cl PAA by NCBI under the condition [NCBI] << [p-Cl PAA] had the following kinetic feature.

### Stoichiometric studies

The stoichiometric studies of oxidation of p-Cl PAA by NCBI were carried out with excess of oxidant (NCBI) and maintaining other parameters constant ($[H^+]$ = 0.15 x 10$^{-3}$ mol dm$^{-3}$, HOAc-H$_2$O = 30 % (v/v), Temperature = 308K). The stoichiometric results indicated 1 mole of p-Cl PAA consumes 1 mole NCBI as represented by the following empirical equation:
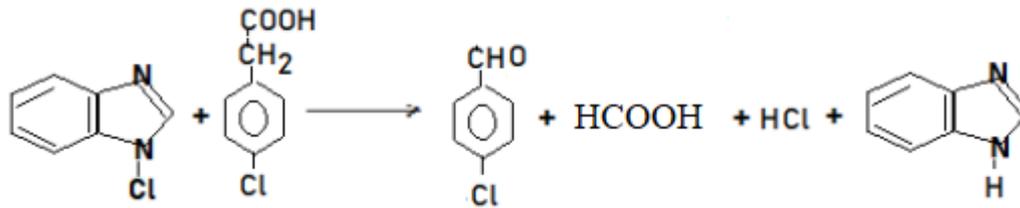
## Order with respect to [oxidant][substrate]

When the p-Cl PAA are in large excess, the plots of log (a-x) vs time **(Figure1)** are found to be linear, indicating first-order dependence on NCBI. The pseudo first-order rate constants in NCBI calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration. Singh et al[11] also reported similar findings. The plot of $k_1$ *vs* [p-Cl PAA] is initially linear passing through origin and tends to obtain limiting value, bending towards horizontal axis **(Figure 2).** Pandey et al[12,13] also published similar reports. Hence the reaction follows fractional order behaviour with respect to the p-Cl PAA concentration.
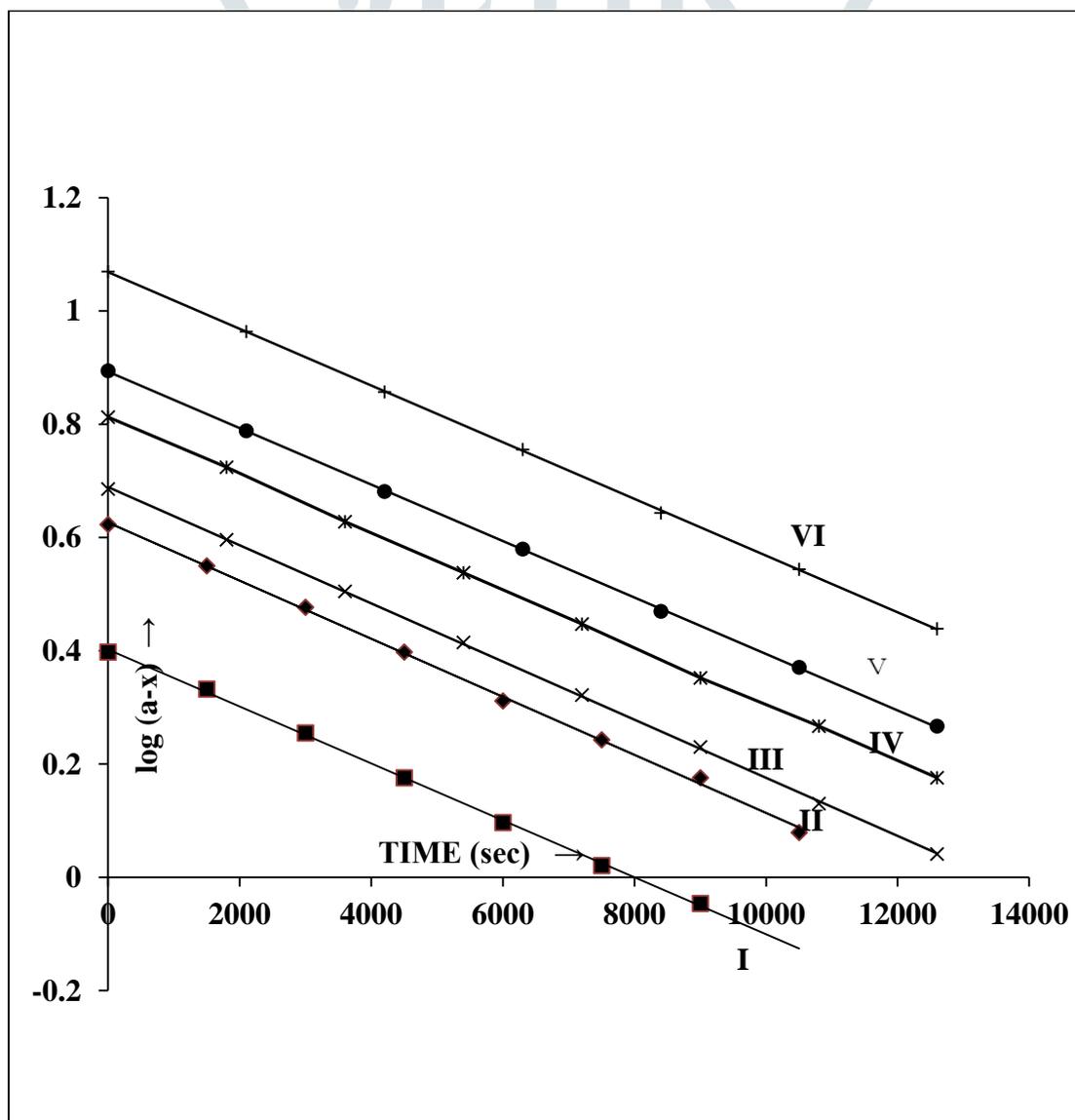


**Figure1:** The plot of log(a-x) versus time. Conditions are given in Table1.
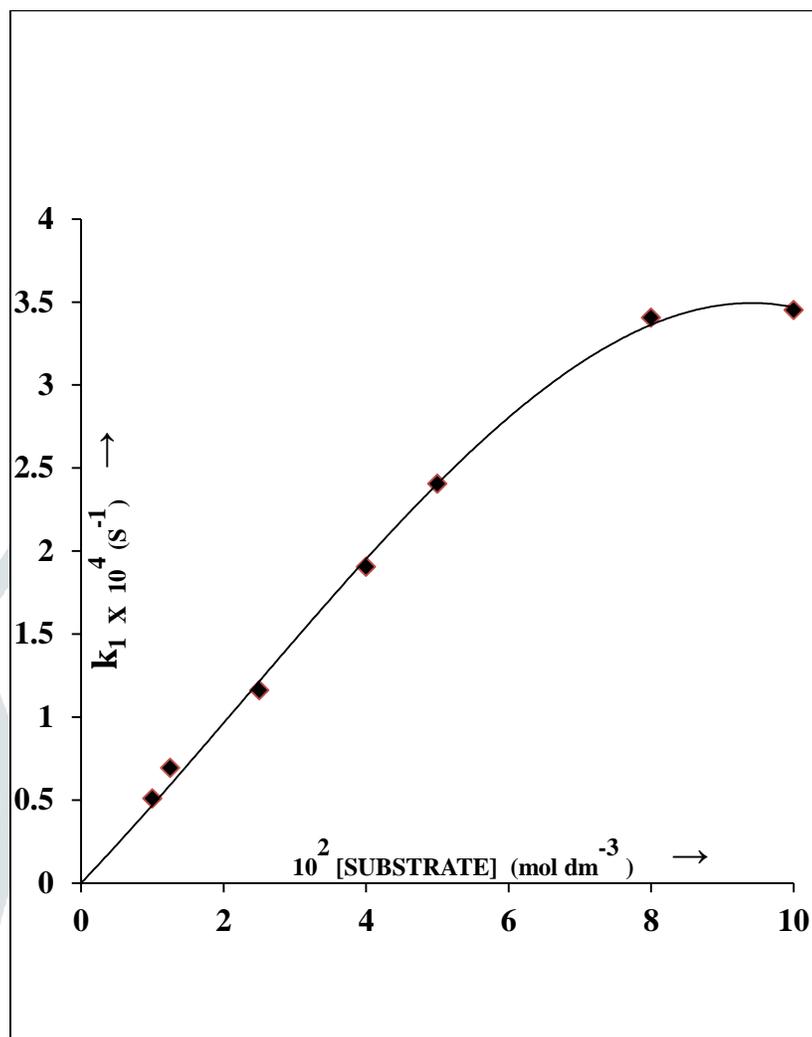
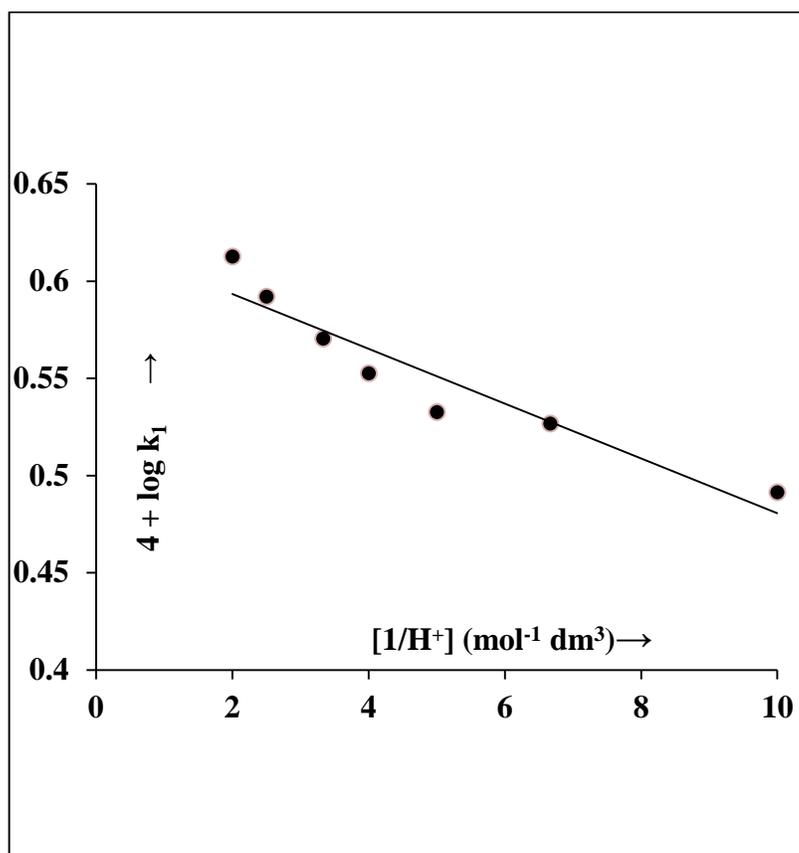**Figure2:** Dependence of $k_1$ on [p-Cl PAA]. Conditions are given in Table 1.

**Table1:** Effect of variation of reactants on pseudo-order rate constant $k_1$ at 308K

| $10^2$[Substrate](mol dm$^{-3}$) | $10^3$[NCBI](mol dm$^{-3}$) | $10^3$[H$^+$](mol dm$^{-3}$) | % HOAc: H$_2$O | $k_1$x$10^4$(s$^1$) |
|---|---|---|---|---|
| 1.0 | 2.5 | 0.15 | 30 | 0.513 |
| 1.25 | 2.5 | 0.15 | 30 | 0.694 |
| 2.5 | 2.5 | 0.15 | 30 | 1.161 |
| 4.0 | 2.5 | 0.15 | 30 | 1.905 |
| 5.0 | 2.5 | 0.15 | 30 | 2.404 |
| 8.0 | 2.5 | 0.15 | 30 | 3.405 |
| 10.0 | 2.5 | 0.15 | 30 | 3.451 |
| 2.5 | 1.5 | 0.15 | 30 | 1.157 |

| 2.5 | 3.0 | 0.15 | 30 | 1.166 |
|-----|-----|------|----|----|
| 2.5 | 4.0 | 0.15 | 30 | 1.163 |
| 2.5 | 5.0 | 0.15 | 30 | 1.166 |
| 2.5 | 7.5 | 0.15 | 30 | 1.162 |
| 2.5 | 2.5 | 0.1 | 30 | 0.953 |
| 2.5 | 2.5 | 0.2 | 30 | 1.259 |
| 2.5 | 2.5 | 0.25 | 30 | 1.342 |
| 2.5 | 2.5 | 0.3 | 30 | 1.425 |
| 2.5 | 2.5 | 0.4 | 30 | 1.586 |
| 2.5 | 2.5 | 0.5 | 30 | 1.723 |
| 2.5 | 2.5 | 0.15 | 10 | 0.852 |
| 2.5 | 2.5 | 0.15 | 20 | 1.015 |
| 2.5 | 2.5 | 0.15 | 40 | 1.351 |
| 2.5 | 2.5 | 0.15 | 50 | 1.647 |

**Effect of variation of [$H^+$]:**

The catalysed kinetics was observed by the addition of hydrochloric acid. On varying hydrochloric acid concentration there is an increase in reaction rate (**Table1**). The plot of log $k_1$ versus 1/[$H^+$] (**Figure 3**) gave a straight line with positive intercept, suggesting that acid plays a complex role in the reaction system. Numerous authors[14-15] have also shown that acid catalyses the rate of the process.

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

**Effect of solvent on reaction velocity:**

The rate was studied at different concentrations of the solvent. It is observed that the rate increase with increasing concentration of acetic acid. The positive slope explains the ion-dipole or dipole-dipole character of the reaction. Kempegowda[16] et al. found a similar tendency in the N-bromoacetamide oxidation of primary alcohols.

**Effect of ionic strength and benzimidazole:**

The pace of oxidation is not appreciably influenced by the addition of chemically neutral salt. Therefore, the ionic behaviour in the slow step and in the reaction mechanism is excluded. Further this trend supporting the dipole-dipole interaction in the reaction. Singh[17] also supported that fact. The pace of reaction is slowed down by adding benzimidazole, one of the reaction products, at constant concentrations of $H^+$, p-Cl PAA, and NCBI. When benzimidazole is added, the reaction rate slows down, indicating a pre-equilibrium stage involving a process where benzimidazole is one of the products. The rate of oxidation should be an inverse function of the concentration of benzimidazole if this equilibrium is engaged in the oxidation process. Some authors[18-19] has observed that reduction products have a similar impact.

### Effect of Product and Free Radical Inhibitor:

The investigated reaction was unable to cause the additional acrylonitrile to polymerize, eliminating the existence of free radicals and their route. Authors came to similar conclusions[20].
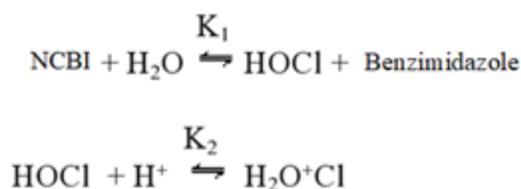
### Effect of temperature:

It was also investigated how temperature affected the way that p-Cl PAA and NCBI worked together. The activation energy values, ΔS, ΔH, and ΔG, were calculated. **Table 2** includes a summary of these values in addition to the other parameters.

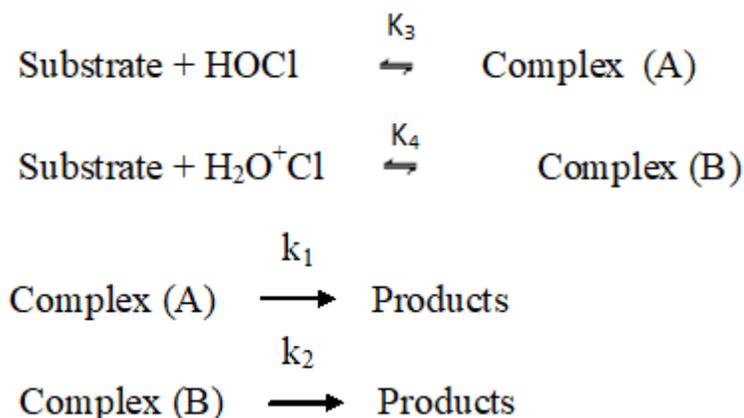### Table2:Thermodynamic parameters of p-Cl PAA-NCBI system

| Substrate | Ea kJ mol$^{-1}$ | A s$^{-1}$ | ΔH$^{\#}$ kJ mol$^{-1}$ | ΔG$^{\#}$ kJ mol$^{-1}$ | - ΔS$^{\#}$ JK mol$^{-1}$ |
|---|---|---|---|---|---|
| p-Cl PAA | 60.467 | $0.98 \times 10^8$ | 57.058 | 88.587 | 77.14 |

## MECHANISM

It was discovered that the NCBI concentration remained steady over time. The development of a complex between the reactive species and p-Cl PAA in a quick step, which would thereafter disintegrate in a long and rate-determining stage, was most likely the mechanism for the reaction. From the list of potential reactive species, the NCBI, $CH_3COOCl$, and $CH_3COO^+HCl$ are not primary reactive species, as demonstrated by the benzimidazole retarding action and the positive effect of $H^+$ and solvent's. As a result, the only option and possibility remaining as a distant prime active species is $HOCl$ and $H_2O^+Cl$. Our kinetic findings published reports also lead us to believe that $HOCl$[21] and $H_2O^+Cl$[22] are the most prevalent and fruitful reactive species. The following mechanism for the oxidative destruction of p-Cl PAA by NCBI is hypothesized based on the above experimental results.

$$NCBI + H_2O \xrightarrow{K_1} HOCl + \text{Benzimidazole}$$

$$HOCl + H^+ \xrightarrow{K_2} H_2O^+Cl$$

$$\text{Substrate} + \text{HOCl} \overset{K_3}{\rightleftharpoons} \text{Complex (A)}$$

$$\text{Substrate} + \text{H}_2\text{O}^+\text{Cl} \overset{K_4}{\rightleftharpoons} \text{Complex (B)}$$

$$\text{Complex (A)} \overset{k_1}{\longrightarrow} \text{Products}$$

$$\text{Complex (B)} \overset{k_2}{\longrightarrow} \text{Products}$$

Using the steady-state treatment with an acceptable approximation hypothesis results in a rate equation capable of describing and justifying all of the observed kinetics, this is eventually calculated as

$$k_{obs}^{-1} = \frac{1}{[S]}\left\{\frac{[BI] + K_1}{K_1(k_1K_3 + k_2K_2K_4[H^+])}\right\} + \frac{K_3}{k_1K_3 + k_2K_2K_4[H^+]}$$

## CONCLUSION

4-chlorophenyl acetic acid is a substituted aliphatic acid. During the reaction, at first, substrate formed a complex with reacting species of NCBI. Similar type of complex formation reported in our previous communications with N-chloroisonicotinamide[23-24]. The study follows Michalis-Menten tpe kinetics with stoichiometry 1:1. The reaction shows first-order rate with respect to oxidant and fractional order with substrate. The kinetic results and thermodynamic parameters support the proposed mechanism.

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