

Kinetics of oxidation of 4-methylphenylacetic acid by N-chlorobenzimidazole

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ABSTRACT

Kinetic data for the rate of oxidation of p-methyl phenylacetic acid p-CH₃PAA with N-chlorobenzimidazole (NCBI) in aqueous acetic acid 30% (v/v) solution in the presence of hydrochloric acid has been carried out. The rate of oxidation is direct function of both [oxidant] and [substrate] in the lower concentration region but tends to be of zero order at higher concentration of the substrates. The increasing trend of H⁺ ions, solvent composition while retarding trend with benzimidazole on the system has been observed. The results thus obtained suggest that the redox process proceeds via formation of an activated transitory complex (1:1) between p-CH₃PAA and postulated reacting specie of NCBI which slowly disintegrates into products. The oxidation products are confirmed and activation parameters have been estimated, and probable course of the reactions path is suggested in consistent with all observed kinetic results.

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

INTRODUCTION

The N-halo oxidant such as NCSA¹⁻³, NBSA⁴⁻⁶, N-chloroisonicotinamide^{7,8}, N-chloronicotinamide^{9,10}, NBS¹¹, NCS¹² etc. have been used for the study of oxidation of various organic substrates. N-chlorobenzimidazole (NCBI) is highly selective, mild and stable oxidizing agent. Kinetics of oxidation of leucine¹³, glycine¹⁴, furfural¹⁵, benzyl alcohol¹⁶, vanillin¹⁷ and cyclanols¹⁸ by NCBI was reported. In this article we report the kinetics of oxidation of p-methyl phenylacetic acid by NCBI in aqueous acetic acid.

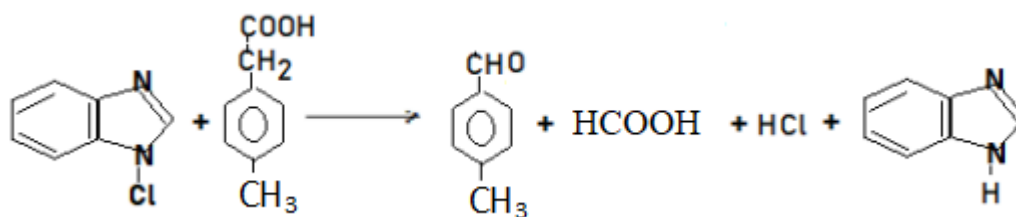
II MATERIALS AND METHODS

Experimental

The sample of NCBI employed in this investigation was prepared in acetic acid. All other chemicals were of AR grade. The solutions used were standardized iodometrically. Demineralized distilled water was used for preparing the solution of hypo, mineral acid and other solutions.

The kinetic analyses were performed using a pseudo first-order approach where the substrate concentrations were in excess and the NCBI concentration was monitored idometrically. In all cases good pseudo first-order kinetics were maintained. The rate data were obtained in the following manner. The required amount of NCBI was kept into a flask, substrate and other reagents taken into another flask. Both flasks are thermostated at ±0.1K (308K). The timer started after the solution of both flasks had been thoroughly mixed. Aliquots were withdrawn at intervals, quenched and analyses idometrically for NCBI.

Product analysis was carried out under kinetic conditions. In a typical experiment, the p-CH₃PAA (0.1) and N-chlorobenzimidazole (0.01) were taken in 100 ml of acetic acid-water (30%), [H⁺] = 0.15 x 10⁻³ mol dm⁻³ and the mixture was allowed to stand in the dark for 12 h to ensure complete reaction. The estimation of residual NCBI in different sets showed that 1mol of substrate consumes 1 mol NCBI according to the stoichiometric equation:



Now remaining mixture was then treated overnight with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine (DNPH) in 2 mol dm⁻³ HCl and kept in a refrigerator. The 2,4-dinitrophenylhydrazone (DNP) precipitate was dried, weighed, and filtered accordingly. Use ethanol to recrystallize the DNP crystal, then weigh it once again. The DNP and DNP of p-CH₃PAA were found to be identical (m.p. 233⁰ C).

RESULT AND DISCUSSION

Under the reaction condition [H⁺] [NCBI] << [p-CH₃PAA] oxidation kinetics has been carried out in binary solvent mixture of the acetic acid and water at 308K.

Order with respect to [oxidant][substrate]

At constant [H⁺] and by keeping substrate in excess, the effect of NCBI concentration on the rate were studied by varying the [NCBI] in the range 1.5 x 10⁻³ to 7.5 x 10⁻³ mol dm⁻³. The plot of log (a-x) versus time was linear indicates first order dependence of the rate on NCBI. The pseudo first order rate constant computed by varying [NCBI] were found constant (**Figure1**) (Table 1). Singh et al¹⁹ also reported similar findings.

The plot of k₁ vs [p-CH₃PAA] is initially linear passing through origin and tends to obtain limiting value, bending towards horizontal axis (**Figure 2**). Pandey et al^{20,21} also published similar reports. Hence the reaction follows fractional order behaviour with respect to the p-CH₃PAA concentration.

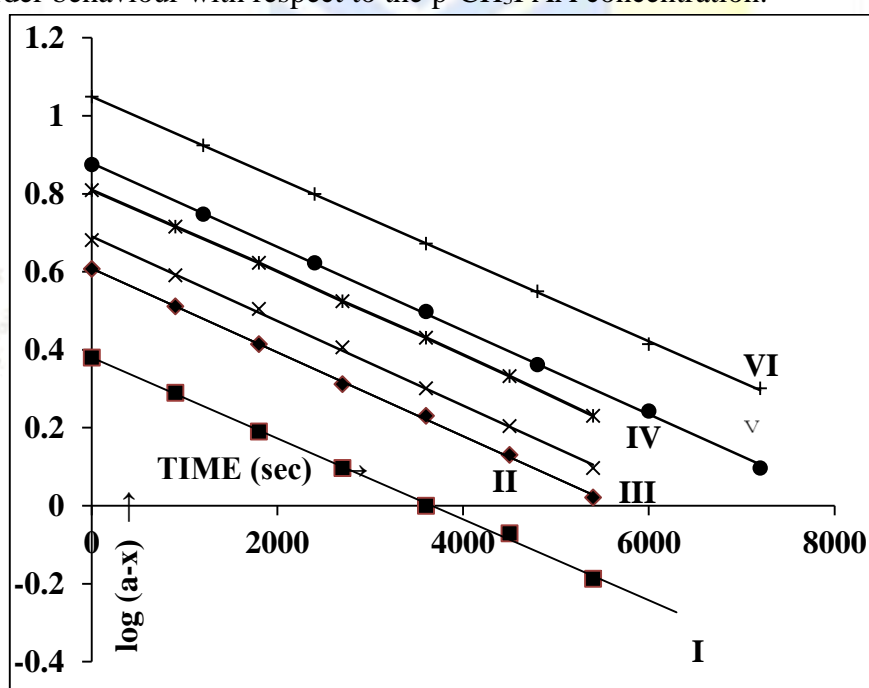


Figure1: The plot of log (a-x) versus time. Conditions are given in Table1.

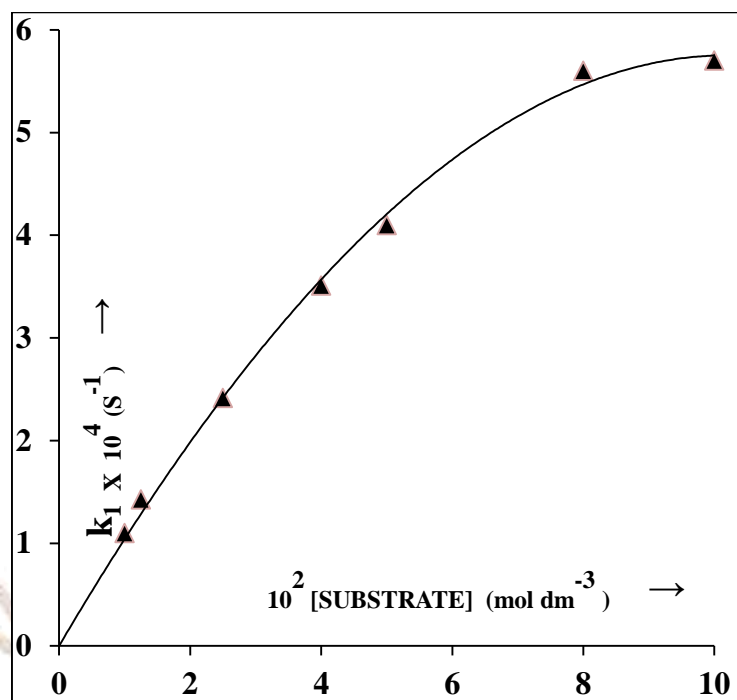


Figure2: Dependence of k_1 on $[\text{p-CH}_3\text{PAA}]$. Conditions are given in Table 1.

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

$10^2[\text{p-CH}_3\text{PAA}](\text{mol dm}^{-3})$	$10^3[\text{NCBI}](\text{mol dm}^{-3})$	$10^3[\text{H}^+](\text{mol dm}^{-3})$	% HOAc: H ₂ O	$k_1 \times 10^4 (\text{s}^{-1})$
1.0	2.5	0.15	30	1.108
1.25	2.5	0.15	30	1.426
2.5	2.5	0.15	30	2.419
4.0	2.5	0.15	30	3.509
5.0	2.5	0.15	30	4.099
8.0	2.5	0.15	30	5.613
10.0	2.5	0.15	30	5.704
2.5	1.5	0.15	30	2.423
2.5	3.0	0.15	30	2.423
2.5	4.0	0.15	30	2.414
2.5	5.0	0.15	30	2.422
2.5	7.5	0.15	30	2.419
2.5	2.5	0.1	30	2.158
2.5	2.5	0.2	30	2.557
2.5	2.5	0.25	30	2.715
2.5	2.5	0.3	30	2.853
2.5	2.5	0.4	30	3.026
2.5	2.5	0.5	30	3.159
2.5	2.5	0.15	10	2.153
2.5	2.5	0.15	20	2.316
2.5	2.5	0.15	40	2.699
2.5	2.5	0.15	50	3.052

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

In order to find the specific acid catalysis experiments were done at constant acetic acid composition but varying the hydrochloric acid concentration from 0.5 to 0.5 mol dm⁻³. It was found that increase in acid concentration increases the rate of reaction and that the order with respect to H⁺ was one (Table 1). 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 authors²²⁻²³ have also shown that acid catalyses the rate of the process.

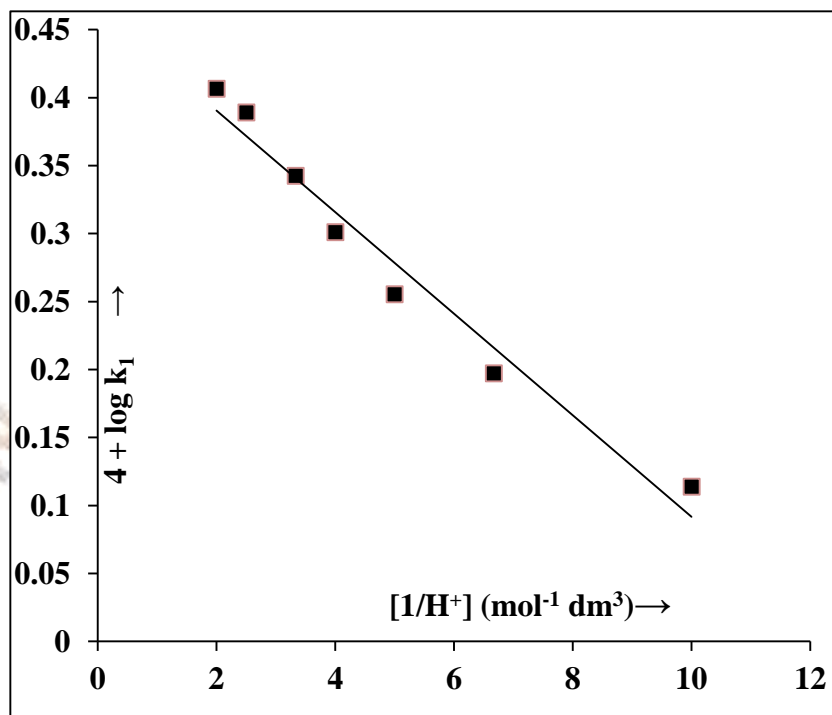


Figure 3: Dependence of $\log k_1$ on $1/[H^+]$. Conditions are given in Table 1.

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. Kempegowda²⁴ et al. found a similar tendency in the N-bromoacetamide oxidation of primary alcohols.

Effect of ionic strength and benzimidazole:

The effect of ionic strength has been studied by varying the concentration of neutral sodium chloride. It was found that there is no substantial change in the reaction rate on varying the ionic strength. It is further supporting the dipole-dipole interaction in the reaction. Singh²⁵ also supported this result in his publication. The pace of reaction is slowed down by adding benzimidazole, one of the reaction products, while the concentrations of other reactants kept constant. When benzimidazole is added, the reaction rate slows down, indicating a pre-equilibrium stage involving a process where benzimidazole is one of the products. Some authors²⁶⁻²⁷ have observed that reduction products have a similar impact.

Effect of Product and Free Radical Inhibitor:

The possibility of radical formation and its involvement in the reaction has been ruled out as the addition of acrylonitrile in the reaction mixture developed no turbidity and hence eliminating the existence of free radicals and their route. Several authors came to similar conclusions^{28,29}.

Effect of temperature:

This oxidation reaction was conducted at four different temperatures viz., 303, 308, 313 and 318 K. Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. The effect of temperature on the reaction of p-CH₃PAA with NCBI were also studied. The value of energy of activation was calculated and the values of ΔS, ΔG were also computed. These values are summarized in Table 2 along with the other parameters.

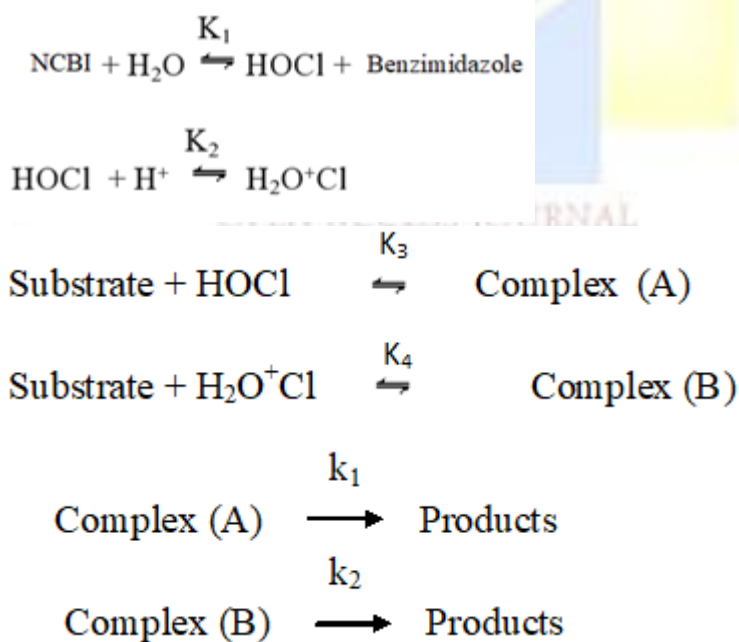
Table 2: Thermodynamic parameters of p-CH₃PAA -NCBI system

Substrate	E _a kJ mol ⁻¹	A s ⁻¹	ΔH [#] kJ mol ⁻¹	ΔG [#] kJ mol ⁻¹	- ΔS [#] JK mol ⁻¹
p-CH ₃ PAA	55.201	1.18 x10 ⁸	61.367	86.634	69.63

MECHANISM

Individual kinetic runs are strictly first-order in NCSA. Further, the first-order rate coefficients do not vary with the initial concentration of the NCBI. The order with respect to the substrate is one but tends to zero at higher concentration. Thus Michaelis-Menten type kinetics is observed with respect to substrate. The overall mechanism therefore involves the formation of an intermediate complex before equilibrium and slow disproportionation of the intermediate in the slow step.

There are long list of potential reactive species, but demonstration of retarding effect by the benzimidazole, increasing effect of H⁺ and solvent's clearly ruled out the NCBI, CH₃COOCl, and CH₃COO⁺HCl as a primary reactive species. So the only option and possibility remaining as a distant prime active species is HOCl and H₂O⁺Cl. Our kinetic findings published reports also lead us to believe that HOCl³⁰ and H₂O⁺Cl³¹ are the most prevalent and fruitful reactive species. On the basis of above kinetic findings, leads to the postulation of the following overall mechanism



Applying the steady state treatment with reasonable approximation hypothesis yields the rate equation capable of explaining and justifying all the observed kinetics finally derived as

$$k_{\text{obs}}^{-1} = \frac{1}{[S]} \left\{ \frac{[BI] + K_1}{K_1 (k_1 K_3 + k_2 K_2 K_4 [H^*])} \right\} + \frac{K_3}{k_1 K_3 + k_2 K_2 K_4 [H^*]}$$

V CONCLUSION

Kinetics studies demonstrate that the binary complex of substrate and oxidant decomposes in a slow rate-determining step to give 4-methylbenzyldehyde as the main product. The experimental stoichiometry is in good agreement. First order to oxidant and fractional order to substrate is supported by derived rate law. The kinetic results and thermodynamic parameters support the proposed mechanism.

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