International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075; Impact Factor: RJIF 5.22
Received: 07-04-2019; Accepted: 10-05-2019
www.chemicaljournals.com
Volume 3; Issue 4; July 2019; Page No. 09-11

Enzyme catalysed oxidation of cinnamic acid by N-bromoisonicotinamide

Aparna Prajapati[1], Arvind Prasad Dwivedi[2], Surendra Singh Parihar[3]
[1] Department of Chemistry, Govt. P.G. Girls College (NAAC), Rewa, Madhya Pradesh, India
[2] Department of Chemistry, Govt. Sanjay Gandhi Smriti Auto. P.G. College, Sidhi, Madhya Pradesh, India

Abstract
The oxidation of cinnamic acid by N-bromoisonicotinamide was carried out in aqueous acetic acid medium. The reaction was catalysed by micelles cetyltrimethylammonium bromide (CTAB). The lone reaction shows first-order rate with oxidant and complex nature of the reaction was observed at its higher concentration. H_2O^+Br was reported as an oxidant species, which attacks to the substrate with stoichiometric ratio 1:2. The rate of reaction increases with increase in binary composition of solvent. The proposed mechanism unconformities with the observed kinetic data and thermodynamic results have been discussed.

Keywords: cinnamic acid, N-bromoisonicotinamide, cetyltrimethylammonium bromide, benzaldehyde, acrylonitrile

1. Introduction

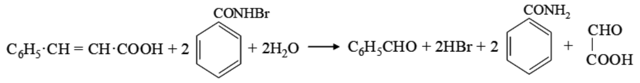
Cetyltrimethylammonium bromide (CTAB) is a micelle enzyme used effectively in various reactions of organic compounds in critical micelle concentration [1]. Aggregation of this surfactant is responsible for altering the rates of organic reaction in aqueous solution, when this compound is dissolved in water, achieves segregation of its hydrophobic portion from the solvent by self-aggregation. It has been reported accordingly by several researchers [2-3] that the micellar enzyme catalyst (CTAB) enhance the rate of reaction and the specificity of the enzyme led to the postulate of a "lock and key" type mechanism [4]. N-bromoisonicotinamide is a stable, versatile halo oxidant. Its potentiality is realized when used in the oxidation of aliphatic alcohols[5] and amino acids.[6] This is very effective oxidant in aqueous medium produces H_2O^+Br oxidizing species which actively participate in the reaction. Recently the kinetics of unsaturated acids by utilizing different oxidizing reagents $KMnO_4$[7], LTA[8] etc. have been reported. The consultation of recent literature reveals that there seems to be no work carried out on the kinetics of aromatic unsaturated acid (cinnamic acid) catalysed by CTAB with NBIN oxidant. Hence we decided to investigate the titled reaction kinetically.

2. Material and Methods

All the reagents used in the foregoing study are of standard grade. The oxidant N-bromoisonicotinamide (NBIN) was prepared in acetic acid. The kinetic study was carried out under the pseudo first order condition [cinnamic acid] >> [NBIN]. The required volumes of cinnamic acid, enzyme (CTAB) and aqueous acid were taken in a glass reaction vessel placed in a thermostat at experimental temperature 313 K. The NBIN solution was also maintained in the same thermostat separately in another flask for 40 minutes. When all the solutions reached to the same equilibrium temperature, the reaction was commenced by mixing of definite amount of NBIN solutions to the first reaction vessel along with enzyme catalyst CTAB. The kinetic reaction was followed by estimating the amount of unreacted NBIN iodometrically at regular intervals of time. The rate constant (k) was calculated by integration and graphical methods respectively.

3. Results and Discussion

The experimental data was collected for the unsaturated cinnamic acid by carrying out oxidation study with halo oxidant, N-bromoisonicotinamide (NBIN) in aqueous acetic acid medium catalysed by enzyme cetyltrimethylammonium bromide, used in critical micelle concentration (CMC) range. The kinetic rate was obtained for the effect of five-fold concentration of NBIN (Table: 1). The analysis of the plot, log (a-x) versus time (Fig.1) with unit slope indicates pseudo-first order with respect to oxidant. The observed rate was determined by varying concentration of cinnamic acid (Table: 2) which shows fractional-order kinetics with respect to substrate which is evidenced by double reciprocal plot of k^{-1} versus [cinnamic acid] $^{-1}$ (Fig.2). The linearity with positive intercept on Y-axis clearly confirms the formation of complex compound in equilibrium at transition state. The study shows that rate of oxidation of cinnamic acid gradually decreases on varying five-fold concentration of $[H^+]$ showing fractional-order kinetics with respect to $[H^+]$ i.e. overall, the rate is unaltered by $[H^+]$. The increase in percentage of composition of acetic acid, increases, the rate of reaction, indicating involvement of dipoles ions in reaction. The influence of neutral salts indicate that the reaction kinetic have insignificant effect on addition of various [NaCl] and [KCl]. The study reveals that at least one of the neutral species involved in the rate determining step in slow process. The addition of various concentrations of oxidation product isonicotinamide inhibits the rate of reaction. The rate increases with increase in concentration of various [CTAB], at optimum concentration, attains almost limiting value of k CTAB fails to catalyse, the reaction at its higher concentration. The plot of k^{-1} versus [CTAB] obtained linear but shows deviation at its higher concentration (Fig. not given). The study fails to establish the presence of free radical in the reaction. The stoichiometry can be represented by the equation as:



The products benzaldehyde and glyoxalic acid was identified by IR-spectroscopic method and also by forming its 2,4-DNP derivatives [9]. Several thermodynamic parameters have been determined which support the mechanism and rate law.

Table 1: Dependence of Rate on the Concentration of Oxidant (NBIN)

$[C_6H_5CH=CH\cdot COOH] = 3.33 \times 10^{-3}$ (mol dm^{-3});
$[CTAB] = 1.50 \times 10^{-3}$ (mol dm^{-3});
$HOAc\text{-}H_2O$ = 50 % (v/v);
Temperature = 313 K

S. No.	[NBIN] × 10^3 (mol dm^{-3})	10^4 k (s^{-1})
1.	1.25	3.58
2.	2.00	3.57
3.	2.50	3.64
4.	3.33	3.61
5.	5.00	3.59

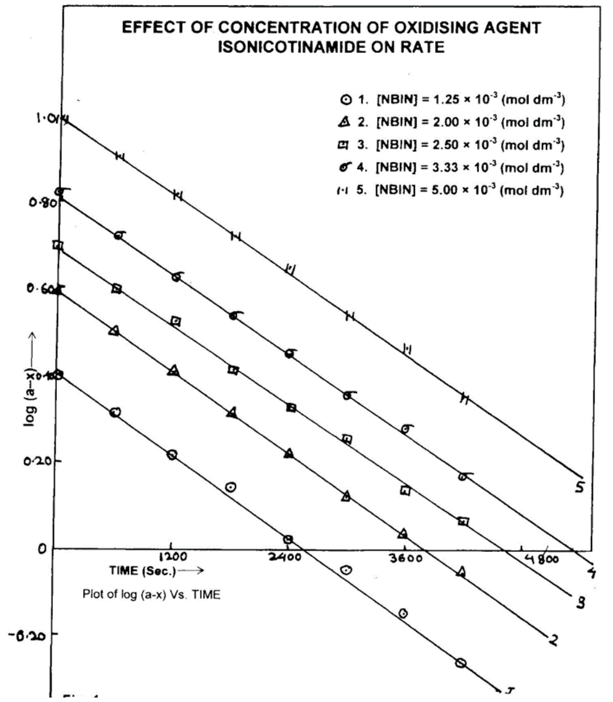


Fig 1: [Cinnamic acid] = 3.33 x 10^{-3}; [CTAB] = 1.50 x 10^{-3} (mol dm^{-3}); HOAc – H_2O = 50% (v/v); Temp. = 313 K

Table 2: Dependence of Rate on the Concentration of Cinnamic acid

[NBIN] = 2.00×10^{-3} (mol dm^{-3});
$[CTAB] = 1.50 \times 10^{-3}$ (mol dm^{-3});
$HOAc\text{-}H_2O$ = 50 % (v/v);
Temperature = 313 K

S. No.	$[C_6H_5CH=CH\cdot COOH]$ × 10^2 (mol dm^{-3})	10^4 k (s^{-1})
1.	1.25	1.88
2.	2.00	2.76
3.	2.50	3.13
4.	3.33	3.64
5.	4.00	3.67
6.	5.00	3.94

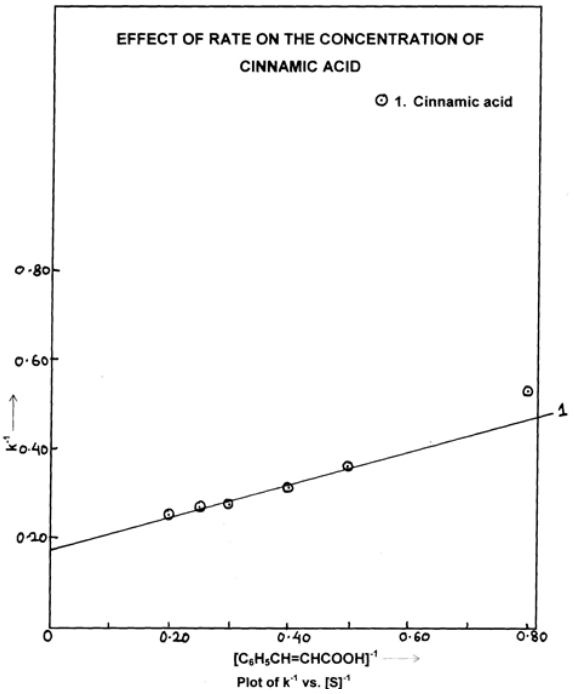
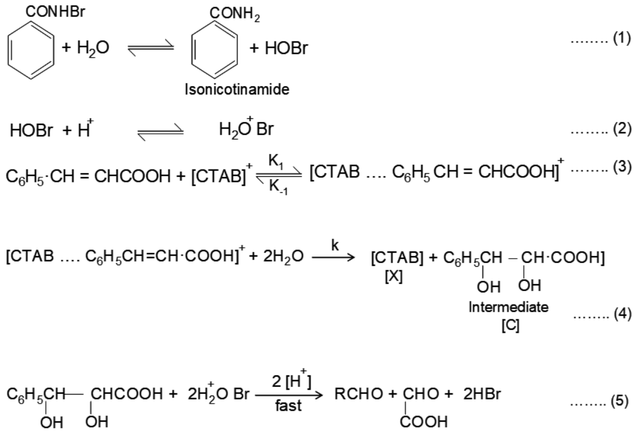


Fig 2: [NBIN] = 2.00 x 10^{-3} (mol dm^{-3}); [CTAB] = 1.50 x 10^{-3} (mol dm^{-3}); HOAc – H_2O = 50% (v/v); Temp. = 313 K

Mechanism

On the basis of kinetic results the mole of mechanism can be proposed in the following pathways:



$$HOBr + H^+ \rightleftharpoons H_2\overset{+}{O}Br \quad \text{........ (2)}$$

$$C_6H_5\cdot CH = CHCOOH + [CTAB]^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [CTAB \text{ .... } C_6H_5CH = CHCOOH]^+ \quad \text{........ (3)}$$

$$[CTAB \text{ .... } C_6H_5CH{=}CH\cdot COOH]^+ + 2H_2O \xrightarrow{k} \underset{[X]}{[CTAB]} + \underset{\substack{\text{Intermediate}\\ [C]}}{C_6H_5\underset{OH}{CH} - \underset{OH}{CH}\cdot COOH]} \quad \text{........ (4)}$$

$$C_6H_5\underset{OH}{CH} - \underset{OH}{CH}COOH + 2H_2\overset{+}{O}Br \xrightarrow[\text{fast}]{2[H^+]} RCHO + \underset{COOH}{CHO} + 2HBr \quad \text{........ (5)}$$

Step (4) is slow and rds of the reaction.
The final rate law was derived as at appropriate condition as:

$$-\frac{d[H_2\overset{+}{O}Br]}{dt} = \frac{[CTAB]_T^+ [S]}{K_1 [S]} \quad \text{........ (6)}$$

The rate equation (6) satisfied all the experimental facts.

4. Conclusion

The limiting value of rate constant (k) for cinnamic acid using enzyme catalyst cetyl- trimethyl ammonium bromide (CTAB) has been determined within CMC range. The existence of complex nature of reaction formed at transition state was explained in mechanism. No decarboxylation occur in the reaction. The final product benzaldehyde was identified by modern physical method and also by forming its 2,4-DNP derivative.

5. References

1. Natarajan Rajagopalan and Siegfried Lindenbaum, J. Lipid Research, Pharm. Chem., USA, 1984, Vol.25.
2. Rama Chandrappa R Puttaswamy Mnyanna, S. M., and MadeGowda, N.B., Int. J. Chem. Kinet. 1998; 30(6):407-414.
3. Porte G, Poggi Y, Appell J, Moret GJ. Phys. Chem. 1984; 88:5703.
4. Michaelis MM, Menton ML. Bio chem. Z. 1913; 49:333.
5. Balasubramaniyan M, Priya V, Mathiyalagam N. Int. J. Chem., Tech. Research Conden (USA). 2011; 3(3):1096-1101.
6. Mathiyalagan N, Balasubramaniyan M, Oriental J. Chem. 2012; 26:1541.
7. Kuyper AC. J Indian Chem. Soc. 1972; 49:625.
8. Adamcikova L, Knappova O. Czechoslovak. Academy of Sciences. 1983; 48:2335.
9. Vogel I. Elementary Prac. Orag. Chem., Pearson Edn. Publ, 2010.