International Journal of Innovation Scientific Research and Review
Vol. 03, Issue, 07, pp.1455-1457, July, 2021
Available online at http://www.journalijisr.com

IJISRR

Research Article

ISSN: 2582-6131

KINETIC AND MECHANISTIC STUDY OF OXIDATION OF NIACIN (VITAMIN-B3) BY SODIUM N-CHLORO TOLUENESULPHONAMIDE (CHLORAMINE-T) IN HCL MEDIUM

[1]R.T.Radhika, [2]Ravi J.D.Saldanha and [3,]* B.M.Venkatesha

[1]Postgraduate Department of Chemistry, Maharani's Science College for women, Mysore, India.
[2]Department of Chemistry, St.Philomena's College, Mysore, India.
[3]Department of Chemistry, Yuvaraja's College, University of Mysore, Mysore India.

Received 14th May 2021; Accepted 15th June 2021; Published online 15th July 2021

ABSTRACT

Kinetic and mechanistic investigation of oxidation of Niacin [Vitamin-B3] using chloramine-T as an oxidant in hydrochloric acid medium has been studied at 303K. Reaction shows a first order dependence of the rate on oxidant [CAT] and Niacin concentration, and inverse fractional order in concentration of hydrochloric acid. Addition of reduction product of chloramine-T toluenesulphonamide , chloride ion, variation of ionic strength and dielectric constant of the medium do not have any significant effect on the rate of the reaction. The activation parameters of the reaction have been computed from the Arrhenius plot. A derived rate law and mechanisms are consistent with obtained experimental results.

Keywords: Niacin(Vitamin-B3), Chloramine-T, Hydrochloric acid medium, Oxidation.

INTRODUCTION

Niacin. also known as pellagra preventive factor (P - P factor) or vitamin B_3 or nicotinic acid . Niacin is one of the most important vitamin which is the physiologically active compound. It plays a vital role in cell respiration, release carbohydrates, fat, and proteins. Deficiency of niacin in human leads to the condition pellagra followed by malfunction of digestive and nervous systems. The literature survey provide information regarding determination of nicotinic acid [1-2], metabolic effect of niacin [3-4]. But reports on kinetic study of reaction of niacin are scanty [5-7]. There is no information available on the reaction with haloamines. As a part of our kinetic and mechanistic studies on the oxidation of substrates by aromatic-N-haloamines [8-10], the present studies were undertaken to investigate the kinetic aspects of reaction of niacin with chloramine-T at 303K in presence of hydrochloric acid.

Experimental:

An aqueous solution of Chloramine-T (E.Merck) was prepared, standardized periodically by iodometric method and preserved in an amber coloured bottle until further use. Analar grade niacin (E.Merck) was used and an aqueous solution of the substrate was prepared. All other chemicals used were of accepted grades purity. The ionic strength of reaction mixture was kept at a high value with concentrated solution of $NaClO_4$ (E Merck).

Kinetic Measurement:

Kinetic runs were performed under pseudo- first order conditions of [Niacin] >> [CAT]. A mixture containing requisite amounts of niacin, $NaClO_4$ and HCl was equilibrated at 303K. To this solution, was added a measured amount of pre-equilibrated (303K) aqueous solution of CAT of known concentration. The progress of the reaction was monitored iodometrically for two half- lives by withdrawing aliquots of the reaction mixture at regular time intervals. The pseudo-first order rate constants calculated were reproducible.

***Corresponding Author: B.M.Venkatesha,**
3Department of Chemistry, Yuvaraja's College, University of Mysore, Mysore India.

Stoichiometry:

Reaction mixture containing different compositions of Niacin and Chloramine -T in reaction conditions were equilibrated at 303K for 48 hours. The iodometric determination of unreacted CAT in the reaction mixture showed that one mole of Niacin consumed one mole of Chloramine -T.

$$C_5H_4NCOOH + ArSO_2NClNa + HCl \longrightarrow C_5H_4NCOOCl + ArSO_2NH_2 + NaCl \quad 1$$

RESULTS:

Kinetics of reaction of Niacin with Chloramine-T (CAT) were investigated at several initial concentrations of the reactants in acid medium. In the presence of excess [Niacin] and fixed [HCl], plots of log [CAT] versus time are linear indicating a first order dependence of rate on $[CAT]_0$. The pseudo-first order rate constants k' are given in (Table-1). The rate increased with increase in [Niacin], (Table-1) plots of log k' versus log [Niacin] were linear with slope 0.62. Thus indicating a fractional order dependence on [Niacin].

Table-1: Effect of varying the reactants concentration on the reaction rate.

[HCl]=2.0x10^{-4} mol dm^{-3} , Temp=303K, μ=0.2 mol dm^{-3}

[CAT]x10^4 mol dm^{-3}	[Niacin]X10^2 mol dm^{-3}	k^{l}X10^6 Sec^{-1}
1.0	4	13.10
1.5	4	13.20
2.0	4	13.30
2.5	4	13.10
3.0	4	13.20
2.0	1	05.66
2.0	2	08.80
2.0	3	11.10
2.0	5	15.18
2.0	6	17.30

At fixed $[CAT]_0$, [Niacin] and temperature, the rate of the reaction decreased with increase in $[HCl]_0$ (Table-2). The plots of log k' versus log [HCl] were linear with negative fractional slope indicating an inverse fractional order of approximately - 0.49 in [HCl].

Table-2 Effect of $[H^+]$ concentration on the rate of reaction.

$[CAT]_0$=2.0X10^{-4} mol dm^{-3}, [Niacin]=4.0X10^{-2} mol dm^{-3} ,Temp=303K , μ=0.2 mol dm^{-3}

[HCl]X10^5 mol dm^{-3}	**k'10^6 sec^{-1}**
10	18.42
15	15.20
20	13.30
25	11.75
30	10.85
35	10.20

The addition of Cl^- ion in the form of NaCl, and ionic strength did not affect the rate. Hence the dependence of the rate on [HCl] reflected the effect of $[H^+]$ only on the reaction. The addition of reaction product of CAT, toluenesulphonamide had no effect on the rate indicating that it is not involved in a pre equilibrium to the rate determining step. Addition of reaction mixture to aqueous acrylamide did not initiate the polymerization showing the absence of free radical species. The reaction was studied at varying temperature 298 K to 313 K from the linear plots. The thermodynamic parameters were computed (Table-3)

DISCUSSION AND MECHANISM:

Chloramine-T ($ArSO_2NClNa$) behaves as a strong electrolyte [11-13] in aqueous solutions and several equilibria exist in acidic conditions.

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+ \quad (2)$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCl \quad (3)$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl \quad (4)$$

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NCl_2 + ArSO_2NH_2 \quad (5)$$

$$HOCl + H^+ \rightleftharpoons H_2^+OCl \quad (6)$$

In acid solutions the probable oxidizing species are the free acid $ArSO_2NHCl$, $ArSO_2NCl_2$, HOCl and H^+_2OCl**.** The involvement of $ArSO_2NCl_2$ in the mechanism leads to a second order rate law according to Eq(5) ,which is contrary to the experimental observations. As Eq (4) indicates a slow hydrolysis, if HOCl were the primary oxidizing species of the first order, a retardation of rate by the added $ArSO_2NH_2$ would be expected. However, no such effect was noticed in the study. Narayanan and Rao[14] and Subhashini etal[15] have reported that monohaloamines can be further protonated at pH< 2 as in Eq (7) for Chloramine-T

$$p\text{-}CH_3C_6H_4SO_2NHCl + H^+ \rightleftharpoons p\text{-}CH_3C_6H_4SO_2N^+H_2Cl \quad (7)$$

In the present case the inverse fractional order in $[H^+]$ suggested that the deprotonation of $ArSO_2N^+H_2Cl$ results in regeneration of $ArSO_2NHCl$ which is likely to be the active species involved in the mechanism of niacin halogenations. Based on the preceding discussion, a mechanism Scheme-1 is proposed for the reaction

.

$$ArSO_2N^+H_2Cl \underset{fast}{\overset{K_1}{\rightleftharpoons}} ArSO_2NHCl + H^+ \quad \text{i}$$

$$ArSO_2NHCl + S \overset{K_2}{\rightleftharpoons} X \quad \text{ii}$$

$$X \underset{slow}{\overset{k_3}{\longrightarrow}} Products \quad \text{RDS} \quad \text{!!!}$$

SCHEME -1

From Scheme -1

$$rate = -\frac{d[CAT]t}{dt} = k_3[X] \quad (8)$$

Then, $$[ArSO_2NHCl] = \frac{[X]}{K_2[S]} \quad (9)$$

$$[ArSO_2N^+H_2\,Cl] = \frac{[ArSO_2NHCl\,][H^+]}{K_1} \quad (10)$$

$$[ArSO_2N^+\,H_2Cl] = \frac{[\,X\,][H^+]}{K_1K_2\,[S\,]} \quad (11)$$

Total effective concentration of CAT from scheme 1 given by eq (12)

$$[CAT]_t = [ArSO_2N^+H_2Cl] + [ArSO_2NHCl] + [X] \quad (12)$$

By substituting for the $[ArSO_2NHCl]$ from eq (9) and for $[ArSO_2N^+H_2Cl]$ from eq (11) into eq (12) and

Solving for [X] one gets $$[X] = \frac{K_1K_2[CAT\,]_t[\,S\,]}{[H^+]+K_1+K_1K_2[\,S\,]} \quad (13)$$

Substituting for [X] in eq (8) leads to the fallowing rate law eq(14)

$$rate = \frac{-d[CAT]_t}{dt} = \frac{K_1K_2k_3[CAT\,]_t[\,S\,]}{[H^+]+K_1+K_1K_2[\,S\,]} \quad (14)$$

The rate law is consistent with the experimental data including first order dependence of the rate on [CAT] , fractional order dependence on [Niacin] and a negative fractional order dependence on [HCl] since the rate = k' $[CAT]_t$, under psendo first –order condition of $[Niacin\,]_0 >> [CAT]_0$, the rate eq (14) can be transformed into eq (15) –(18)

$$k' = \frac{K_1K_2k_3[S]}{K_1+[H^+]+K_1K_2[\,S\,]} \quad (15)$$

$$\frac{1}{k'} = \frac{1}{K_2k_3[S]} + \frac{[H^+]}{K_1K_2k_3[S]} + \frac{1}{k_3} \quad (16)$$

or

$$\frac{1}{k'} = \frac{1}{K_2k_3[S]}\left\{\frac{K_1+[H^+]}{K_1}\right\} + \frac{1}{k_3} \quad (17)$$

or

$$\frac{1}{k^1} = \frac{[H^+]}{K_1K_2k_3[S]} + \left\{\frac{1}{K_2k_3[S]} + \frac{1}{k_3}\right\} \quad (18)$$

Based on eq (17) a plot of $\frac{1}{k'}$ versus $\frac{1}{[S]}$ **[fig-1]** at constant [H], $[CAT]_0$ and temperature was found to be linear (r > 0.9989). Similarly from eq (18) a plot of $\frac{1}{k'}$ versus $[H^+]$ **(fig-2)** at constant [S], $[CAT]_0$ and temperature was linear. The values of K_1, K_2 and k_3 were calculated (K_1=2.63× 10^{-4} mol dm^{-3}, K_2=21.726 dm^3 mol^{-1} , k_3 = 2.127× 10^{-5} s^{-1}). The protonation constant in the reaction

condition $K_P=\frac{1}{K_1}$ (K_P=3789.39 dm^3 mol^{-1}) of $ArSO_2NHCl$ can be evaluated.

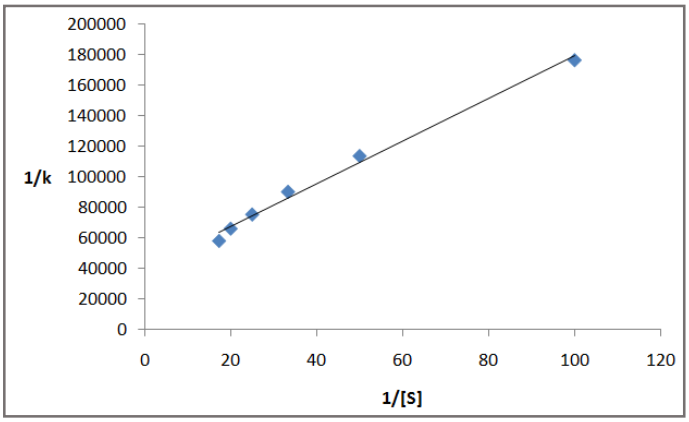

Fig-1.Plot of 1/k^' vs 1/([S]), [CAT]0=2.0X10-4 mol dm-3, [NA]=4.0X10-2 mol dm-3 , [HCl]=2.0x10-4 mol dm-3, Temp=303K, μ=0.2 mol dm-3

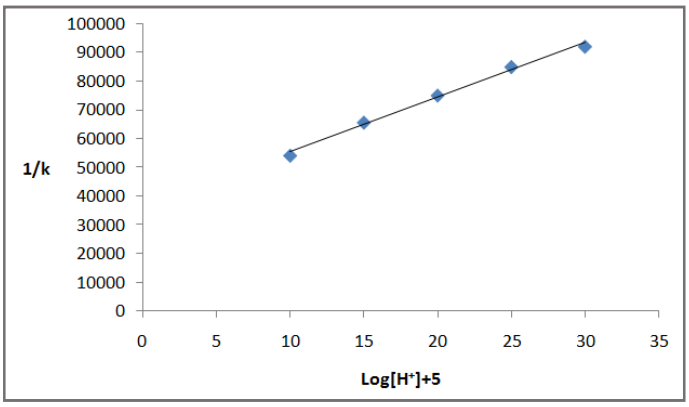

Fig-2. Plot of $\frac{1}{k'}$ vs $[H^+]$,$[CAT]_0$ = 2.0X10^{-4} mol dm^{-3} [NA]=4.0X10^{-2} mol dm^{-3}, [HCl]=2.0x10^{-4} mol dm^{-3}, Temp=303K, μ=0.2 mol dm^{-3}

The thermodynamic parameters Ea, ΔH# Δs#, and ΔG# have been calculated, as shown in Table-3. The moderate value of enthalpy of activation (ΔH#) is supportive of the proposed mechanism in Scheme-1 The highly negative value entropy of activation (Δs#) indicates the formation of rigid transition state by an associative process.

Table-3: **Temperature dependence and activation parameters for the reaction of niacin with Chloramine-T,**

$[CAT]_0$=2.0X10^{-4} mol dm^{-3},[HCl]=2.0x10^{-4} mol dm^{-3}, [Niacin]=4.0X10^{-2} mol dm^{-3} μ=0.2 mol dm^{-3}

Temp in K	k^{I}x10^6 sec^{-1}	Activation parameters
298	09.45	Ea = 54.057 KJmol^{-I}
303	13.30	ΔH# = 51.516 KJ mol^{-I}
308	19.19	ΔS# = -168.530 JK^{-I}mol^{-I}
313	26.61	ΔG# = 103.004 kJ mol^{-I}

REFERENCES

1. Capellu peiro E, Monferrer-pons L; Garca-Alvarez-Coque C: Estere-Romero J **Analytical chimica Acta** 427(1), 93-100(2001)
2. Seemab Khan, M K Rai, V K Gupta and J K Rai , **Ind J chem**. **44A**, 98-101 (2005)
3. Weiwang, Alice Basinger, Richard A Neele, Mark Christiansen and Mark K Hellerstein. **Am J physiol, Endocrinol.metab , 280(3)**, E 540- 547(2001)
4. Ronald B Goldberg and Terry A Jacobson **Mayoclin Proc. 83** (4), 470-478 (2008)
5. Weiang, Alice Basinger, Richard A Neele, Mark Christiansen and Mark K Hellerstein. **Am J physiol, Endocrinol.metab** , **279(1)**, E 50(2000)
6. A.Dayalan and V R Vijayaraghavan **Ind. J. Chem 40A**, 959 (2001)
7. Bondureva V M Orchinnikova EV Andrushkevich TV **React.Kiinet and Cot Lett, 94(2)** 327- 335 (2005)
8. D S Mahadevappa, s Ananda. A S A Murthy and K S Rangappa **Tetrahedron 10**, 1673 (1984)
9. B M Venkatesha, S Ananda and D S Mahadevappa **Ind.J.Chem 30A** 789-792 (1991)
10. S.Ananda, B M Venkatesha, D S Mahadevappa, N M Made gowda **Int.J.Chem Kenet 25**,755-770 (1993)
11. Pryde B G Soper F G, **J.Chem, Soc 2158** (1926) 1514 (1931)
12. Morris J C Slaazar J A and Wineman M A. **J. Amc.Chem.Soc.70**, 2036(1948)
13. Bishop E and Jennings V.J. **Talanta 1**. 197 (1958)
14. Narayanan S S and Rao V R S **Radiochem. Acta 32** 211 (1983)
15. M.Subhashini M Subramanian and V R S Rao **Talanta 32**, 1082 (1985)

Authors biography :

Dr. R.T.Radhika.

Dr. R.T.Radhika has obtained her Ph.D., degree in Chemistry in the year 2000 from the University of mysore, and joined as Assistant professor in Chemistry in department of colligiate education Karnataka government. At present she is the Assistant professor (Selection Grade) in post graduate department of Chemistry, Maharani's Science College for women ,Mysore. She has served as Head of the department of Chemistry, Govt. First grade college, K.R.Nagar, and member of the BOS and BOE University of Mysore and other Universities and Autonomous colleges. She has published more than 20 research papers in reputed journal and presented the 22 papers in national and international conferences .

Dr.Ravi J D Saldanha

Dr.Ravi J D Saldanha completed his Ph.D. degree in Chemistry from University of Mysore , joined as Lecturer in Chemistry . At present he is the Associate professor of Chemistry, He was published 8 research papers in reputed journals.

Dr. B.M.Venkatesha Communicating author

Dr. B.M.Venkatesha obtained his Ph.D., degree in Chemistry in the year 1994 from the University of mysore, and joined as Lecturer in Chemistry at University of Mysore. At present working as Professor of Chemistry, Department of Chemistry , Yuvaraja's College, University of Mysore. He has served as Head of the department of Chemistry, Controller of Examinations, Chairmen and member of the BOS and BOE Yuvaraja's College, University of Mysore and other Universities and Autonomous colleges. He has published more than 45 research papers in reputed journal and presented the 30 papers in national and international conferences .

****