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KINETIC STUDY OF OXIDATION OF NICOTINIC ACID (VITAMIN-B_3) BY SODIUM N-CHLORO BENZENE SULPHONAMIDE (CHLORAMINE-B) IN HYDROCHLORIC ACID MEDIUM

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ABSTRACT
Kinetic and mechanistic investigation of Nicotinic acid [Vitamin-B3] using chloramine-B as oxidant in hydrochloric acid medium has been studied at 303 K. Reaction shows a first order dependence of the rate on oxidant [CAB] and Nicotinic acid concentration, and inverse fractional order in concentration of hydrochloric acid. The reaction rate shows inverse fractional order on reduction product of chloramine-B, benzenesulphonamide concentration. Addition of 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 consistent with obtained experimental results.

KEYWORDS: Vitamin-B3, Chloramine-B, Hydrochloric acid medium, Oxidation Kinetic study.

INTRODUCTION
Aromatic N-halosulphonamides are mild oxidants containing a strongly polarized N-linked halogen in its +1 oxidation state. The prominent member of this group, chlroamine-T (CAT) is a well known analytical reagent and the mechanistic aspects of many of its reaction have been documented.[1-4] Chloramine-B (CAB) (p-$C_6H_5SO_2NClNa.3H_2O$) is a halo-amine containing a positive chlorine has been introduced as an oxidimetric titrant in aqueous medium.

Nicotinic acid (niacin) is also known as pellagra-preventive factor (p-p factor) or vitamin-B3. Niacin is one of the most important vitamin, it plays a vital role in cell respiration, release carbohydrates, fat and proteins, and normal secretion of bile. Deficiency of nicotinic acid in human leads to the condition pellagra followed by malfunction of digestive and nervous system. The literature survey provides information regarding the determination of nicotinic acid and metabolic effects of nicotinic acids.[5-8] The reports on kinetic study of reactions of nicotinic acid are scanty.[9-11] Kinetic and mechanistic study of chromium (VI) catalyzed oxidation, bioremediation of hydrocarbon, hydrogenation of cyclopentene without catalyst and in the presence of molybdenum disulfide.[12-14] Hence we are reporting a kinetic investigation of vitamin-B3 with chloramine-B in presence of hydrochloric acid at 303K.

MATERIAL AND METHODS
Experimental: Chloramine-B (CAB) was prepared using a standard method and its purity checked iodometrically and through IR and NMR spectral data.[15] An aqueous solution of CAB was prepared, standardized by iodometric method and preserved in amber colored bottle until use, to prevent its photochemical deterioration.

Analar grade niacin (E-Merck) was used and aqueous solution of the substrate was prepared. All other chemicals used were of accepted grades of purity. The ionic strength of reaction mixture was kept at a high value by adding required amount of concentrated $NaClO_4$ solution. Triply distilled water was employed for preparing aqueous solutions.

Kinetic Measurements: Kinetic runs were performed under pseudo-first order condition of [nicotinic acid] >> $[CAB]_0$. Mixture containing requisite amount of solutions of the niacin, $NaClO_4$ and HCl were taken in a stopperd pyrex glass tubes whose outer surfaces were coated black to eliminate photochemical effects. A

required amount of water was added to maintain constant total volume for all runs. The reaction vessel was thermostated in a water bath set at a temperature 303K. To this solution a measured amount of pre-equilibrated CAB solution was added to give a 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. Under pseudo-first order conditions, rate constants k′ were reproducible with in ± 3%. The regression analysis of experimental data was carried out on an origin 5.0 by HP 7540 computer.

Stoichiometry and Product Analysis: Investigations under the conditions [CAB] >> [vitamin-B3] revealed that two moles of CAB were consumed by one mole of substrate. The stoichiometry of oxidation is illustrated by following equation.

$$C_5H_4NCOOH + 2PhSO\,NCl^- Na^+ + 2H_2O \rightarrow C_5H_5NO_2 + 2PhSO_2NH_2 + CO_2 + Na^+ + Cl^- \quad (1)$$

The reaction product of CAB, benzene sulphonamide was identified by TLC using petroleum ether-chloroform-1-butanol (2:2:1 v/v) solvent system for ascending irrigation and iodine as developing reagent (Rf = 0.88).The 2,5,-dihydroxy pyridine present in the reaction mixture was identified with authenticated sample by TLC method. Further it was confirmed by conventional ferric chloride test.[16] The evolved CO_2 was detected by the conventional lime water test. Attempts to quantitative measure of the CO_2 evolved were unsuccessful.

RESULTS AND DISCUSSION

The reactions were performed in the presence of HCl under pseudo-first order condition of [nicotinic acid] >>[CAB]0, gave a linear plots of log [CAB] verses time. The linearity of these plots, together with the constancy of the slope for various [CAB]0 indicates a first order dependence of the reaction rate on [CAB]. The pseudo-first order rate constants k′ obtained at 303K are listed in table-1. Under the same experimental conditions an increase in [nicotinic acid]0 increased the rate were given in table- 1 and figure-1 . The plots of log k′ verses log [nicotinic acid] were linear with slope ≈1.0 thus indicating a first order dependence on [nicotinic acid].

Table-1: Effects of varying reactant concentrations on the reaction rate [HCl] = 2.5 x 10^{-4} mol dm^{-3}; Temp = 303 K ; μ = 0.2 mol dm^{-3}

[CAB]x10^4 mol dm^{-3}	[NA]x10^2 mol dm^{-3}	K'x10^5 sec^{-1}
1.26	2.0	2.58
1.73	2.0	2.52
2.00	2.0	2.50
2.43	2.0	2.48
2.86	2.0	2.54
2.00	0.5	0.75
2.00	1.0	1.20
2.00	1.5	1.82
2.00	2.0	2.50
2.00	2.5	3.20
2.00	3.0	4.21

The addition of Cl^- or Br^- ions in the form of NaCl or NaBr at constant $[H^+]$ did not affect the rate. Hence the dependence of the rate on [HCl] reflected the effect of $[H^+]$ only on the reaction. At constant[Nicotinic acid], and [CAB] reaction was studied with varying concentration of HCl at 303K (table-2), the plots of logk′ vs log [HCl] (figure-2) were linear(r>.9968) with negative slope indicating inverse fractional order dependence of rate on H^+ ion concentration.

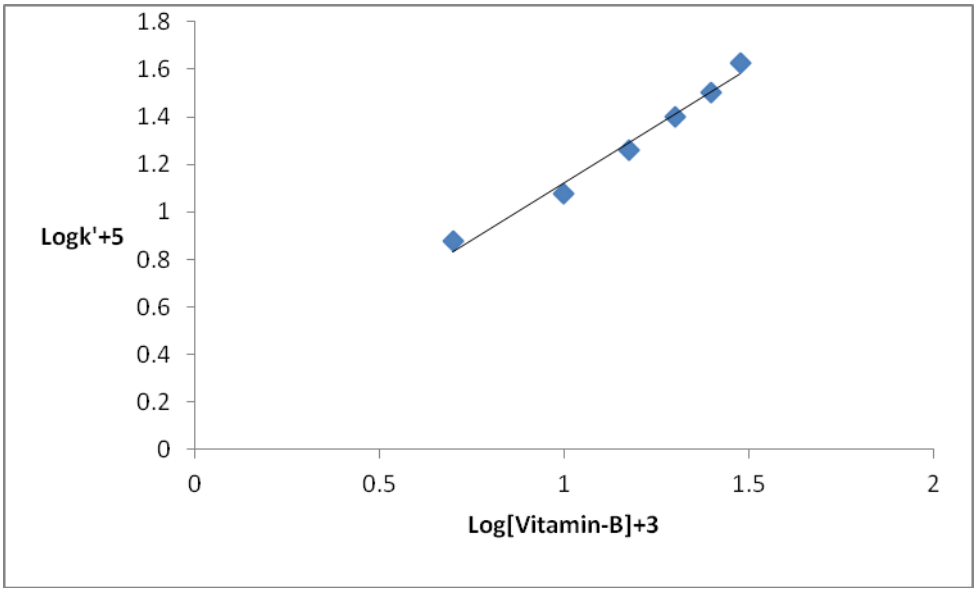

Figure-1: Plot of logk'vs log[Vitamin-B].

As shown in table-2. Addition of reaction product benzenesulphonamide (5.0 x10^{-5}-25.0 x10^{-5} mol dm^{-3}) to the reaction mixture retarded the reaction rate. Further the plots of log k′ vs log [BSA] were linear (r > 0.9993) (figure.1) with negative fractional slope (≈ –0.75). The variation of ionic strength of the medium had no effect on the reaction rate. Addition of reaction mixture to aqueous acrylamide did not initiate the polymerization, showing the absence of free radical species. The reactions were studied at varying temperatures from 298K to 313K, from the linear plots the activation parameter were computed are given in table-3.

Table-2: Effects of varying [HCl] on the reaction rate [NA] = 2.0 x 10^{-2}mol dm^{-3}; [CAB]0 = 2.0×10^{-4} mol dm^{-3}; Temp = 303K ; μ= 0.2 mol dm^{-3}.

[HCl]x10^{4} mol dm^{-3}	K'x10^{5} sec^{-1}
1.0	5.10
1.5	4.20
2.0	3.30
2.5	2.50
3.5	1.81
4.5	1.21

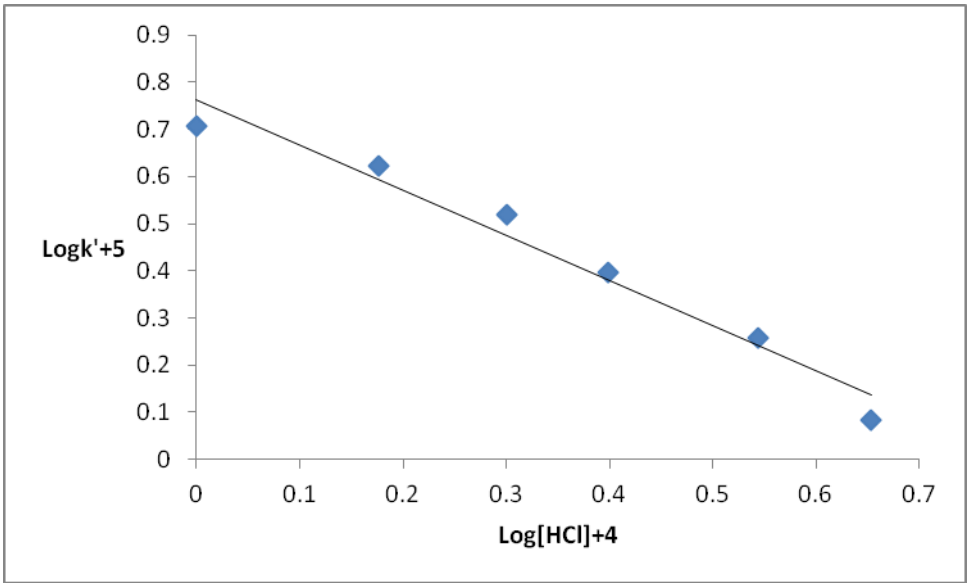

Figure-2: Plot of logk' vs log [HCl].

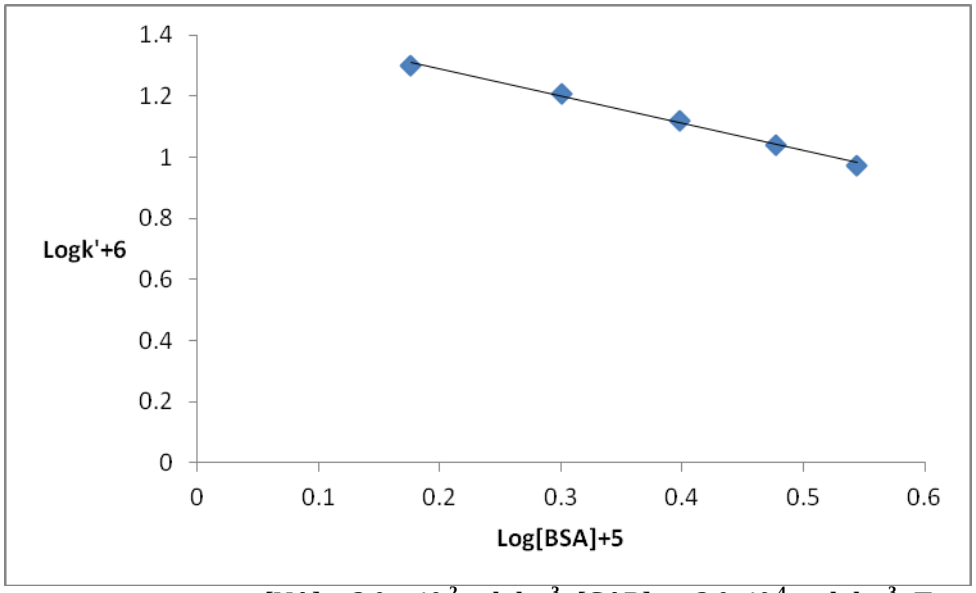

Figure 3: Plot of log [BSA] vs logk' [NA] = 2.0 x 10^{-2}mol dm^{-3}; [CAB]0 = 2.0×10^{-4} mol dm^{-3}; Temp = 303K ; μ= 0.2 mol dm^{-3}.

Mechanism

Chloramine-B (PhSO2NClNa) like chloramine-T behaves as a strong electrolyte in aqueous solutions forming different species as shown in Equation2-6.[17-19]

$$PhSO_2NClNa \rightleftharpoons PhSO_2NCl^- + Na^+ \quad (2)$$

$$PhSO_2NCl^- + H^+ \rightleftharpoons PhSO_2NHCl \quad (3)$$

$$PhSO_2NHCl + H_2O \rightleftharpoons PhSO_2NH_2 + HOCl \quad (4)$$

$$2PhSO_2NHCl \rightleftharpoons PhSO_2NH_2 + PhSO_2NCl_2 \quad (5)$$

$$HOCl + H^+ \rightleftharpoons H_2O^+Cl \quad (6)$$

In acid solutions, the probable oxidizing species are the free acid PhSO2NHCl, PhSO2NHCl2, HOCl and H2O+Cl. The involvement of PhSO2NCl2 in mechanism leads to a second-order rate law according to equation (5), which is contrary to the experimental observations. The monohaloamines can be further protonated at $P^H < 2$ as in equation (7) and (8) for chlroamine-T and chlroamine-B respectively.[20,21]

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

$$C_6H_5SO_2NHCl + H^+ \rightleftharpoons C_6H_4SO_2N^+H_2Cl \quad (8)$$

Therefore in acidic conditions, for chloramine-B, $PhSO_2NHCl$ is expected to protonate as follows.

$$C_6H_5SO_2NHCl + H^+ \rightleftharpoons C_6H_5SO_2N^+H_2Cl \quad (9)$$

In the present study of oxidation of vitamin-B3 , the inverse fractional order in [H+] suggests that the deprotonation of PhSO2N+H2Cl results in formation of PhSO2NHCl, as shown in step (i) and in step (ii) the PhSO2NHClundergo hydrolysis with the formation of active oxidizing species HOCl with the elimination of PhSO2NH2, as the inverse fractional order with [PhSO2NH2] was observed. Further the reaction rate shows dependence of first order on [vitamin-B3], indicating HOCl is reacting with the substrate with slow step and gives products on the subsequent steps. Based on the preceding discussion a mechanism scheme 1is proposed to account for the experimental observations.

$$PhSO_2N^+H_2Cl \underset{fast}{\overset{K_1}{\rightleftharpoons}} PhSO_2NHCl + H^+ \quad (i)$$

$$PhSO_2NHCl + H_2O \underset{fast}{\overset{K_2}{\rightleftharpoons}} HOCl + PhSO_2NH_2 \quad (ii)$$

$$HOCl + S \xrightarrow{k_3} X \quad \text{Slow} \quad (iii)$$

$$X + HOCl \xrightarrow{k_4} \text{Products} \quad (iv)$$

Scheme-1

Rate= -d[CAB]/dt =k_3[HOCl][S] . ..... (10)

Total effective concentration of CAB for scheme 1 given by equation (11)

$$[CAB]_t = [PhSO_2N^+H_2Cl] + [PhSO_2NHCl] + HOCl \quad (11)$$

and solving for [HOCl] gets

$$[HOCl] = \frac{K_1K_2[H_2O][CAB]_t}{[PhSO_2NH_2][H^+] + K_1[PhSO_2NH_2] + K_1K_2[H_2O]} \quad (12)$$

Substitution for [HOCl] in equation (11) we get the rate law equation (13)

$$Rate = \frac{-d[CAB]_t}{dt} = \frac{k_3K_1K_2[CAB]_t[S][H_2O]}{PhSO_2NH_2\{[H^+] + K_1\} + K_1K_2[H_2O]} \quad (13)$$

Table-3: Temperature dependence and activation parameters for the reaction of Niacin with Chloramine-B [NA] = 2.0×10^{-2}mol dm^{-3} [CAB] = 2.0×10^{-4} mol dm^{-3} [HCl] =2.5×10^{-4} mol dm^{-3} Temp. = 303 K μ = 0.2 mol dm^{-3}

Temp. in K	K'x10^5 sec^{-1}	Thermodynamic parameters
298	1.56	Ea=65.542 kJ mol^{-1}
303	2.50	$\Delta H^{\#}$=62.976 kJ mol^{-1}
308	3.75	$\Delta S^{\#}$= -125.76 JK^{-1}
313	5.65	$\Delta G^{\#}$=101.46 kJ mol^{-1}
318	7.80	---

The rate law is consistent with the experimental observation of first order in [CAB] and [vitamin-B3], and fractional order in [H^+]. The energy of activation Ea, and thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ were calculated as shown in table 3. The moderate value of enthalpy of activation ($\Delta H^{\#}$) is supportive of the proposed mechanism in scheme 1. The high negative value of entropy of activation ($\Delta S^{\#}$) indicates the formation of a rigid transition state by associative process.

REFERENCES

1. Mahadevappa D.S., Ananda S., Murthy ASA., and Rangappa K.S., *Tetrahedron*, 1984; 10: 1673.
2. Rao P.V.S., Subbaiah K.V., and Murthy PSN. *React Kinet*, Catol, Lett., 1979; 10: 79.
3. Venkatesha B.M., Ananda S., Mahadevappa D.S., *Indian J. Chem*, 1991; 30A: 789-792.
4. Ananda S., Venkatesha B.M., Mahadevappa D.S., Madegowda N.M. *Int J. Chem Kinet*, 1993; 25: 755-770.
5. Capella-Peiro E., Monferrer-ponsL., Garca-Alvarez-CoqueC., Esteve-Romeroj. *Analytical chimica Acta*, 2001; 427: 193-100.
6. Seemabkhan M.K. Rai., Gupta U.K., and Rai J.K., *Indian Journal of chemistry*, 2005; 44A 98-101.
7. Wei Wang., Alice Basinger., Richard A. Neese, Barryshane,Su-A Myong., Mark Christiansen and Marc K Hellerstein., *Am.J. Physiol Endocrinal, metab*, 2001; 280(3): 540-547.
8. Ronald B. Goldberg., and Terry A. Jacobson., *Mayoclin Proc*, 2008; 83(4): 470- 478.
9. Wei Wang., Alice Basinger., Richard A Neese., Mark Christiansen and Marc K., Heller stein., *Am.J. P. Physiol. Endocrinal. Metab*, 2000; 279(1): 50.
10. Dayalan A., and R.Vijayaraghvan V., *Indian J. Chem* 40A, 2001; 959.
11. Bundareva VM., Ovchinnikava EV., and rushkevich TV., *React Kinet, and Cat Lett*, 2008; 94(2): 327-335.
12. Sonawane Vilas Y. *Res.j.chem.sci.*, 2011; 1(1): 25-30.
13. Medjor O.W, Egharevba F., Akpoveta O.V., Ize-Iyamu O.K. and Jatto E.O. *Res.j.chem.sci.*, 2012; 2(1): 38-44.
14. Atohoun Y.G.S., Kuevi U.A., Kpota A.H. and Mensah J.B., *Res.j.chem.sci.*, 2011; 1(8): 18-23.
15. Ahmed M.S., Mahadevappa D.S., Talanta, 1980; 27: 669.
16. Furniss B.S., Hannatord. A.J., Smith P.W.G., & Tatchell.A.R., Vogels Text book of organic chemistry,Pearson Publication, 2009; 1213.
17. Pryde B.G., Soper F.G., *J chem., Soc.*, 1931; 1582(1926): 1514.
17. Morris J.C., Salazar J.A., and Wineman M.A., *J. Ame, Chem soc*., 1948; 70: 2036.
18. Bishop E., and Jennings V.J., Talanta, 1958; 1: 197.
19. Narayanan SS., and RaoV.R.S ., *Radiochem, Acta*, 1983; 32: 211.
20. Subhashini M., Subramanian M., and Rao V.R.S., Talanta, 1985; 32: 1082.