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RESEARCH ARTICLE

RUTHENIUM (III) CATALYSED OXIDATION OF NIACIN BY CHLORAMINE-B IN HYDROCHLORIC ACID MEDIUM: A KINETIC STUDY

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ABSTRACT

The kinetics of oxidation of Niacin by sodium-N-chlorobenzenesulphonamide (CAB) has been studied in HCl medium with Ru (III) as catalyst at 303 K. The reaction rate shows first order dependence on both [substrate] and [oxidant], fractional order dependence on [Ru (III)] and inverse fractional order on both [HCl] and [BSA]. Addition of halide ions, variation of ionic strength and dielectric constant of the medium do not have any significant effect on the rate of 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.

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INTRODUCTION

The chemistry of chloramines has attracted the attention of many investigators on account of nature of the chemistry of N-halo amines, their ability to act as source of halonium cations, hypolite species and N-anions, which act both as bases and nucleophiles (Kolavari et al., 2007). These compounds contain positive halogen and are mild oxidants (Nanda, 2011). They interact with a wide range of functional groups, affecting a variety of molecular transformation. A prominent member of this class is chloramine-B (CAB, $C_6H_5SO_2NClNa.1.5H_2O$) is a stable compound and is found to be better oxidizing agent than its analogue CAT (Nanda et al., 1998; Ananda et al., 1995; Kondarasaiah et al., 2002; Chandrashekar et al., 2012). Niacin is also known as pellagra-preventive factor (p-p factor) or vitamin-B_3. 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 niacin 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 (Capella-Peiro et al., 2001; Khan Seemab, 2005; Wei Wang et al., 2001; Ronald et al., 2008). The reports on kinetic study of reactions of niacin are scanty (Wei Wang et al., 2000; Dayalan, 2001; Bundareva et al., 2008). Hence we are reporting a kinetic investigation of Niacin (vitamin-B_3) with chloramine-B in presence of hydrochloric acid with Ru (III) catalyst at 303K.

Experimental: Chloramine-B (CAB) was prepared using a standard method and its purity checked iodometrically and through IR and NMR spectral data (Ahmed, 1980). 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. A solution of $Rucl_3.3H_2O$ (Arora matthey) in 0.5 M HCl was prepared and used as the stock catalyst solution.

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Allowance was made for the amount of HCl present in the catalyst solution while preparing reaction mixtures for kinetic runs. 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 used 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, $NaClO_4$, Ru(III) and HCl were taken in a stoppered pyrex glass tubes whose outer surfaces were coated black to eliminate photochemical effects. A required quantity 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 computer.

Stoichiometry and Product Analysis

Varying ratios of oxidant, substrate in the presence of HCl medium, ruthenium chloride catalyst were equilibrated at 303K for 24 hours. The unchanged oxidant in the reaction mixture was determined by iodometric titration. The analysis showed that one mole of niacin reacted with two mole of oxidant, according to the following stoichiometry, forming 2, 5, dihydroxy pyridine.

$$C_5H_4NCOOH + 2PhSO_2NCl^-Na^+ + 2H_2O \rightarrow C_5H_5NO_2 + 2PhSO_2NH_2 + CO_2 + Na^+ + Cl^- \quad (1)$$

The reaction product benzene sulphonamide (PhSO2NH2) was detected by TLC using light petroleum ether-chloroform-1-butanol (2:2:1 v/v) as the solvent and iodine, the detection agent solvent system for ascending (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 (Furniss et al., 2009). The evolved CO2 was detected by the conventional lime water test. Attempts to quantitative measure of the CO2 evolved were unsuccessful.

RESULTS

The stoichiometry of the Niacin-CAB reaction was found to be 1:2 ratio. The reaction performed in the presence of Ru (III) and HCl under pseudo-first order conditions of [Niacin]>>[CAB], gave linear plots of log[CAB] versus time. The linearity of these plots, together with the constancy of the slope at 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 [Niacin]0 increased the rate were given in table 1. The plots of log k versus log [Niacin] were linear with slope ≈1.0 thus indicating a first order dependence on [Niacin].

Table-1. Effects of varying reactant concentrations on the reaction rate
[HCl] = 2.5 x 10^{-4} mol dm^{-3} ; [Ru(III)]= 6.215 x 10^{-6} mol dm^{-3}; Temp. = 303 K; μ = 0.2 mol dm^{-3}

[CAB] x 10^4 mol dm^{-3}	[NA] x 10^2 mol dm^{-3}	k′ x 10^5 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 [Niacin], and [CAB] reaction was studied with varying concentration of HCl at 303K, the plots of log k′ vs log [HCl] were linear (r>0.9968) with negative slope indicating inverse fractional order dependence of rate on $[H^+]$ as shown in figure 1 . The rate increased with increase in [Ru(III)] and plot of log k′ vs [Ru(III)] was linear with slope equal to 0.6 indicating fractional order on Ru(III) 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 [$RuCl_2$] on the reaction rate [NA] = 2.0 x 10^{-2}mol dm^{-3}; $[CAB]_0$ = 2.0×10^{-4} mol dm^{-3}; [HCl] = 2.5 x 10^{-4} mol dm^{-3} ; Temp. = 303K; μ= 0.2 mol dm^{-3}

[$RuCl_2$]x10^6 mol dm^{-3}	k′ x 10^5 sec^{-1}
1.243	0.61
2.486	1.18
3.729	1.72
4.972	2.15
6.215	2.50
7.458	4.00

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}; [Ru(III)]= 6.215 x 10^{-6} mol dm^{-3}; Temp. = 303 K; μ = 0.2 mol dm^{-3}

Temp. in K	k′ x 10^5 sec^{-1}	Thermodynamic parameters
298	1.20	Ea = 63.860 kJ/mol
		$\Delta H^{\neq}$ = 61.297 kJ/mol
303	2.50	$\Delta S^{\neq}$ = -132.09 JK^{-1}/mol
308	3.60	$\Delta G^{\neq}$ = 101.98 kJ/mol
313	5.12	
318	7.23	

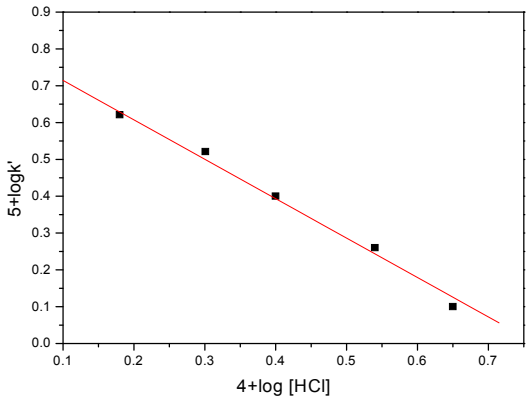

Figure-1, Plot of logk′ vs [HCl] [NA] = 2.0 x 10^{-2}mol dm^{-3}; $[CAB]_0$ = 2.0×10^{-4} mol dm^{-3}; [Ru(III)]= 6.215 x 10^{-6} ; Temp. = 303K; μ= 0.2 mol dm^{-3}

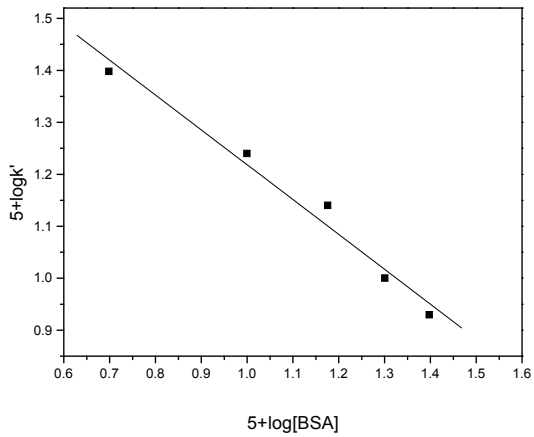

Figure-2. Plot of logk′ vs [BSA] [NA] = 2.0 x 10^{-2}mol dm^{-3}; $[CAB]_0$ = 2.0×10^{-4} mol dm^{-3}; [Ru(III)]= 6.215 x 10^{-6} ; Temp. = 303K; μ= 0.2 mol dm^{-3}

DISCUSSION AND MECHANISM

Chloramine-B ($PhSO_2NClNa$) like chloramine-T behaves as a strong electrolyte in aqueous solutions forming different species as shown in Equation 2-6 (Pryde, 1926; Morris, 1948; Bishop, 1958).

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

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

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

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

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

In acid solutions, the probable oxidizing species are the free acid $PhSO_2NHCl$, $PhSO_2NHCl_2$, HOCl and H_2O^+Cl. The involvement of $PhSO_2NCl_2$ 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 pH < 2 as in equation (7) and (8) for chlroamine-T and chlroamine-B respectively (Narayanan, 1983; Subhashini, 1985).

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

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

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

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

Electronic spectral studies have shown that coordination species such as $[RuCl_5(H_2O)]^{-2}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{+2}$ do not exist in the aqueous solution of $RuCl_3$. Ruthenium (III) however exists in the following ligand substitution equilibrium in acid medium (Cady, 1958; Connick, 1960; Davtokratova, 1963; Griffith, 1967; Backhours, 1950).

$$[Ru(III)Cl_6]^{3-} + H_2O \rightleftharpoons [Ru(III)Cl_5(H_2O)]^{2-} + Cl^- \quad (10)$$

The above equilibrium was used in ruthenium (III) chloride catalyzed oxidation of primary alcohols by BAB and ethylene glycols by N-bromoacetamide in $HClO_4$ medium (Singh, 1984; Singh, 1988). In the present study however, the chloride ion has no effect on the rate which indicates that the complex ion $[RuCl_6]^{3-}$ is the reactive catalyst species, that interacts with the niacin to form a complex intermediate, similar results were observed in the Ru(III) catalyzed oxidation of chloro acetic acids by bromamine-T (BAT) (Ananda, 1993) and bromamine-B.

In the present study the oxidation of Niacin in the presence of Ru(III) as catalyst, the inverse fractional order in $[H^+]$ suggest that, the deprotonation of $PhSO_2N^+H_2Cl$ in step (i) results in the formation of regeneration of $PhSO_2NHCl$. A retardation by the added benzenesulphonamides ($PhSO_2NH_2$) i.e. an inverse fractional order on $[PhSO_2NH_2]$ indicates hydrolysis of monobromamine $[PhSO_2NHCl]$ to form HOCl in step (ii) which act as the active species in fast pre- equilibrium step. The reaction rate shows fractional order in Ruthenium(III) concentration and first order on [Niacin]. Based on the preceding discussion a mechanism scheme 1 is proposed to account for the experimental observation.

Scheme-1 leads to the rate law as follows

$$\text{Rate} = \frac{-d[CAB]_t}{dt} = k_4'[X][S] \quad (11)$$

$$K_1' = \frac{[PhSO_2NHCl][H^+]}{[PhSO_2N^+H_2Cl]} \quad (12)$$

$$K_2' = \frac{[HOCl][PhSO_2NH_2]}{[PhSO_2NHCl][H_2O]} \quad (13)$$

$$K_3' = \frac{[X]}{[HOCl][Ru(III)]} \quad (14)$$

Total effective concentration of CAB for scheme 1 given by equation (15)

$$[CAB]_t = [PhSO_2N^+H_2Cl] + [PhSO_2NHCl] + [HOCl] + X \quad (15)$$

From equilibria (i), (ii) and (iii) in scheme 1

$$[HOCl] = \frac{[X]}{K_3'[Ru(III)]} \quad (16)$$

$$[PhSO_2NHCl] = \frac{\frac{[HOCl][PhSO_2NH_2]}{K_{2'}}}{\frac{[X]}{K_3'[Ru(III)]}\frac{[PhSO_2NH_2]}{K_2'}}$$

$$[PhSO_2NHCl] = \frac{[HOCl][PhSO_2NH_2]K_3'[Ru(III)]K_2'}{[X][PhSO_2NH_2]K_{2'}} \quad (17)$$

$$[PhSO_2N^+H_2Cl] = \frac{\frac{[PhSO_2NHCl]\,[H]^+}{K_1'}}{\frac{[X][PhSO_2NH_2]\,[H]^+}{K_1'K_2'K_3'[Ru(III)]}}$$

$$[PhSO_2N^+H_2Cl] = \frac{[PhSO_2NHCl]\,[H]^+ K_1'K_2'K_3'[Ru(III)]}{K_1'[X][PhSO_2NH_2]\,[H]^+} \quad (18)$$

By solving for $[CAB]_t$ of equation (15) and equations (16 to 18), one gets,

$$CAB]_t = [X]\left[\frac{[PhSO_2NH_2][H]^+}{K_1'K_2'K_3'[Ru(III)} + \frac{[PhSO_2NH_2]}{K_2'K_3'[Ru(III)} + 1\right] \quad (19)$$

$$= \left[\frac{[PhSO_2NH_2][H]^+ + K_1'[PhSO_2NH_2] + K_1'K_2' + K_1'K_2'K_3'[Ru(III)]}{K_1'K_2'K_3'[Ru(III)]}\right] \quad (20)$$

$$[X] = \frac{K_1'K_2'K_3'[Ru(III)][CAB]_t}{[PhSO_2NH_2][H]^+ + K_1'[PhSO_2NH_2] + K_1'K_2' + K_1'K_2'K_3'[Ru(III)} \quad (21)$$

$$\text{Rate} = \frac{k_4'K_1'K_2'K_3'[Ru(III)][CAB]_t[S]}{[PhSO_2NH_2]\{[H^+] + K_1'\} + K_1'K_2'[1 + K_3'[Ru(III)]} \quad (22)$$

This rate law equation (22) is in agreement with the experimental observations, including a first order in [CAB], an inverse fractional order in $[H^+]$ and [BSA] and a fractional order in [Ru(III)]. The thermodynamic parameters Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ were calculated as shown in table 3. The moderate value of enthalpy of activation ($\Delta H^{\neq}$) is supportive of the proposed mechanism in scheme 1. The high negative value of entropy of activation ($\Delta S^{\neq}$) indicates the formation of a rigid transition state by associative process.

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