Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **2(8),** 26-30, August **(2012)** *Res.J.Chem.Sci.*

Kinetics of Oxidation of Vitamin-B_3 (Niacin) by Sodium N-bromo benzenesulphonamide (Bromamine-B) in HCl Medium and Catalysis by Ru(III) ion

Chandrashekar[1], Venkatesha B.M.[1*] and Ananda S.[2]
[1]Department of Chemistry, Yuvaraj's college, University of Mysore, Mysore -570005, INDIA
[2]Department of studies in Chemistry, Manasagangothri, University of Mysore, Mysore, INDIA

Available online at: www.isca.in
Received 18th April 2012, revised 30th April 2012, accepted 3rd May 2012

Abstract

Kinetics of uncatalyzed and Ru(III) catalyzed oxidation of vitamin-B_3 (niacin) by the titled compound (bromamine-B) in HCl medium has been studied at 303K. The uncatalyzed reaction shows a first order dependence of the rate on (BAB) and (vitamin-B_3), inverse fractional order in (acid). The Ru(III) Catalyzed reaction on the other hand shows a first order behavior on each of (BAB) and (vitaminB_3), fractional order dependence on Ru(III) and inverse fractional order in (acid). The reaction rate shows inverse fractional order (benzenesulphonamide) in both uncatalyzed and Ru(III) ion catalyzed reactions. Addition of halide ions, variation of ionic strength and dielectric constant of the medium had no effect on the reaction rate. Activation parameters have been evaluated from the arrhenius plots, mechanisms consistent with the above kinetic data have been proposed.

Keywords: Vitamin-B_3, bromamine-B, oxidation, Ru (III), catalysis.

Introduction

Aromatic N-halo sulphonamides 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[1,2,3,4]. Bromamine-B (BAB) (p-$C_6H_5SO_2NBrNa.3H_2O$) is a halo-amine containing a positive bromine has been recently introduced as an oxidimetric titrant in aqueous medium.

Nicotinic acid (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 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-B_3 with bromamine-B in presence of hydrochloric acid at 303K.

Material and Methods

Experimental: Bromamine-B (BAB) was prepared using a standard method and its purity checked iodometrically and through IR and NMR spectral data[15]. An aqueous solution of BAB 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. 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 employed for preparing aqueous solutions.

Kinetic Measurements: Kinetic runs were performed under pseudo-first order condition of (niacin) >> $(BAB)_0$. Mixture containg requisite amount of solutions of the niacin, $NaClO_4$, Ru(III) (in case of catalyzed reaction only) 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 BAB 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 [BAB] >> [vitamin-B_3] revealed that two moles of BAB were consumed by one mole of substrate. The stoichiometry of oxidation is illustrated by following equation.

$$C_5H_4NCOOH + 2PhSO_2NBr^-Na^+ + 2H_2O \rightarrow$$
$$C_5H_5NO_2 + 2PhSO_2NH_2 + CO_2 + Na^+ + Br^- \quad (1)$$

The reaction product of BAB, benzenesulphonamide 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

Uncatalyzed Reaction: The reactions were performed in the presence of HCl under pseudo-first order condition of (niacin) >>$(BAB)_0$, gave a linear plots of log (BAB) verses time. The linearity of these plots, together with the constancy of the slope for various $(BAB)_0$ indicates a first order dependence of the reaction rate on (BAB). 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′ verses 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 [Ru (III)] = 6.215 x 10^{-6} mol dm^{-3}; [HCl] = 2.5 x 10^{-4} mol dm^{-3} ;Temp = 303 K ; μ = 0.2 mol dm^{-3}

[BAB] x 10^4 mol dm^{-3}	[NA] x 10^2 mol dm^{-3}	k′ x 10^4 Sec^{-1}
1.26	2.0	6.14 (0.541)
1.73	2.0	6.52 (0.560)
2.00	2.0	6.06 (0.558)
2.43	2.0	6.65 (0.574)
2.86	2.0	6.39 (0.531)
2.00	0.5	1.58 (0.142)
2.00	1.0	3.16 (0.310)
2.00	1.5	4.89 (0.446)
2.00	2.0	6.06 (0.558)
2.00	2.5	7.80 (0.758)
2.00	3.0	9.77 (0.851)

*The values in the parenthesis are for the uncatalyzed oxidation of niacin by BAB in HCl medium.

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. Addition of reaction product benzenesulphonamide (5.0 x10^{-5}-30.0 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 > 0.9907) with negative fractional slope (≈ – 0.62). 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.

Ru(III) Catalyzed Reaction: The reaction performed in the presence of Ru(III), under pseudo-first order condition of (vitamin-B_3) >> $(BAB)_0$ gave a linear plots of log (BAB) vs time (r > 0.9988), indicating a first order dependence of the reaction rate on (BAB), as in the uncatalyzed reaction. The values of k′ were given in table 1. When the variables kept constant, the rate increased with increase in (vitamin-B_3) (r > 0.9989) and obtained a unit slope indicates a first order rate dependence on the substrate concentration. At constant $(vitamin\text{-}B_3)_0$, (BAB) and [Ru(III)], the reaction was studied with varying concentration of HCl at 303K, the plots of log k′ vs. log [HCl] were linear (r > 0.9924) with negative fractional slope indicating inverse fractional order (≈ – 0.51) dependence of rate H^+ ion concentration and shown in table 2.

Table-2
Effects of varying [HCl] on the reaction rate [NA] = 2.0 x 10^{-2}mol dm^{-3}; $[BAB]_0$ = 2.0×10^{-4} mol dm^{-3} ; [Ru (III)] = 6.215 x 10^{-6} mol dm^{-3} ; Temp = 303K ; μ= 0.2 mol dm^{-3}

[HCl]x10^4 mol dm^{-3}	k′ x 10^4 sec^{-1}
1.0	9.40 (0.871)
1.5	7.61 (0.725)
2.0	6.70 (0.635)
2.5	6.06 (0.558)
3.5	5.10 (0.478)
4.5	4.30 (0.381)

*The values in the parenthesis are for the uncatalyzed oxidation of niacin by BAB in HCl medium.

Runs performed with increasing [Ru(III)], keeping other conditions constant, showed an increase in the rate. The slopes of the linear plots of log k′ vs log [Ru(III)] indicates fractional order (≈ 0.6) dependence of the rate on Ru(III) concentration as shown in figure 1.

Addition of reaction product benzenesulphonamide (5.0 x10^{-5}-30.0 x10^{-5} mol dm^{-3}) to the reaction mixture retarded the reaction rate. Further, the plot of log k′ vs log (BSA) was linear (r > 0.9958) with negative fractional slope (≈ – 0.62).

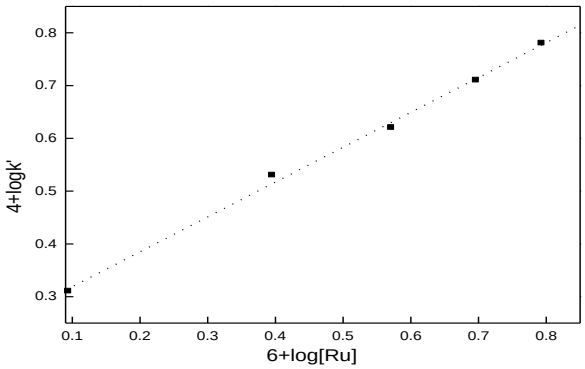

Figure-1

Plot of log k′ vs log [Ru(III)]. [NA] = 2.0 x 10^{-2}mol dm^{-3} ;[BAB]$_0$ = 2.0 ×10^{-4} mol dm^{-3}; [HCl] = 2.5 ×10^{-4} mol dm^{-3};μ= 0.2 mol dm^{-3}; Temp = 303K

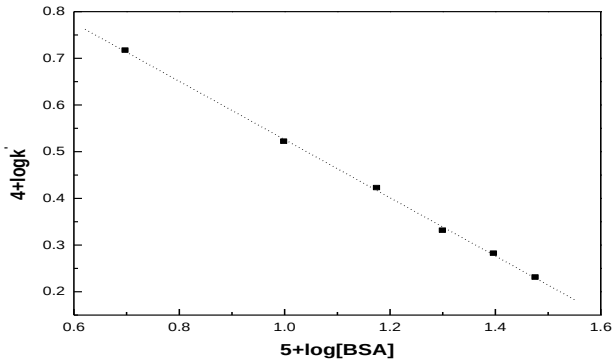

Figure-2

Plot of log k′ vs log [BSA]. [NA] = 2.0 x 10^{-2}mol dm^{-3}; [BAB]$_0$ = 2.0 ×10^{-4} mol dm^{-3}; Ru(III) = 6.215×10^{-6} mol dm^{-3}; [HCl] = 2.5 ×10^{-4} mol dm^{-3}; μ= 0.2 mol dm^{-3}; Temp = 303K

Addition of Cl^- or Br^- ions in the form of NaCl and NaBr and variation of ionic strength by adding $NaClO_4$ had no influence on the reaction rate in the presence of Ru (III) as catalyst. Test performed using aqueousacryl amide monomer for the presence of free radicals in the reaction mixture was found to be negative.

Mechanism: Bromamine-B ($PhSO_2NBrNa$) like its chlorine analog chlroamine-B and chlroamine-T behaves as a strong electrolyte in aqueous solutions forming different species as shown in Equation2-6[17,18,19].

$$PhSO_2NBrNa \rightleftharpoons PhSO_2NBr^- + Na^+ \quad (2)$$

$$PhSO_2NBr^- + H^+ \rightleftharpoons PhSO_2NHBr \quad (3)$$

$$PhSO_2NHBr + H_2O \rightleftharpoons PhSO_2NH_2 + HOBr \quad (4)$$

$$2PhSO_2NHBr \rightleftharpoons PhSO_2NH_2 + PhSO_2NBr_2 \quad (5)$$

$$HOBr + H^+ \rightleftharpoons H_2O^+Br \quad (6)$$

In acid solutions, the probable oxidizing species are the free acid $PhSO_2NHBr$, $PhSO_2NHBr_2$, HOBr and H_2O^+Br. The involvement of $PhSO_2NBr_2$ 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[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 bromamine-B, $PhSO_2NHBr$ is expected to protonate as follows.

$$C_6H_5SO_2NHBr + H^+ \rightleftharpoons C_6H_5SO_2N^+H_2Br \quad (9)$$

Uncatalyzed Reaction: In the present study of oxidation of vitamin-B_3 in the absence of Ru(III) catalyst, the inverse fractional order in $[H^+]$ suggests that the deprotonation of $PhSO_2N^+H_2Br$ results in formation of $PhSO_2NHBr$, as shown in step (i) and in step (ii) the $PhSO_2NHBr$ undergo hydrolysis with the formation of active oxidizing species HOBr with the elimination of $PhSO_2NH_2$, as the inverse fractional order with $[PhSO_2NH_2]$ was observed. Further the reaction rate shows dependence of first order on [vitamin-B_3], indicating HOBr is reacting with the substrate with slow step and gives products on the subsequent steps. Based on the preceding discussion a mechanism scheme 1 is proposed to account for the experimental observations.

$$PhSO_2N^+H_2Br \underset{fast}{\overset{K_1}{\rightleftharpoons}} PhSO_2NHBr + H^+ \quad (i)$$

$$PhSO_2NHBr + H_2O \underset{fast}{\overset{K_2}{\rightleftharpoons}} HOBr + PhSO_2NH_2 \quad (ii)$$

$$HOBr + S \xrightarrow{K_3} X \quad \text{Slow} \quad (iii)$$

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

Scheme-1

From the slow step of the preceding sheme1

$$Rate = \frac{-d[BAB]}{dt} = Rate = k_3[HOBr][S] \quad (10)$$

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

$$[BAB]_t = [PhSO_2N^+H_2Br] + [PhSO_2NHBr] + HOBr \quad (11)$$

and solving for [HOBr] gives equation (12)

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

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

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

The rate law is consistent with the experimental observation of first order in (BAB) and (vitamin-B_3), and fractional order in $[H^+]$.

Ru(III) catalyzed reaction: 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 $[RuCl_5(H_2O)_5]^{2+}$ do not exist in the aqueous solution of $RuCl_3$. Ruthenium (III) however exists in the following ligand substitution equilibrium in acid medium[22-26].

$$[Ru(III)Cl_6]^{3-} + H_2O \rightleftharpoons [Ru(III)Cl_5(H_2O)]^{2-} + Cl^- \quad (14)$$

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[27,28]. In the present study however, the chloride ion has no effect on the rate which indicates that the complex ion $[RuCl_3]^{3-}$ is the reactive catalyst species, simillar results were observed in the Ru(III) catalyzed oxidation of chloroacctic acids by bromamine-T (BAT)[29] and bromamine-B. In the present study the oxidation of vitamin-B_3 in the presence of Ru(III) as catalyst, the inverse fractional order in $[H^+]$ suggest that, the deprotonation of $PhSO_2N^+H_2Br$ in step(i) results in the formation of regeneration of $PhSO_2NHBr$. A retardation by the added benzene sulphonamides ($PhSO_2NH_2$) i.e.an inverse fractional order on $[PhSO_2NH_2]$ indicates hydrolysis of monobromamine $[PhSO_2NHBr]$ to form HOBr in step (ii) which act as the active species in fast pre- equilibrium step. The reaction rate shows fractional order in Ru(III) concentration and first order on [vitamin-B_3]. Based on the preceding discussion a mechanism scheme 2 is proposed to account for the experimental observation.

$$PhSO_2N^+H_2Br \overset{K_1'}{\rightleftharpoons} PhSO_2NHBr + H^+ \quad \text{(i)}$$

$$PhSO_2NHBr + H_2O \overset{K_2'}{\rightleftharpoons} HOBr + PhSO_2NH_2 \quad \text{(ii)}$$

$$HOBr + Ru(III) \overset{K_3'}{\rightleftharpoons} X \quad \text{(iii)}$$

$$X + S \xrightarrow{k_4'} X^{\cdot} + Ru(III) \quad \text{slow} \quad \text{(iv)}$$

$$X^{\cdot} + HOBr \xrightarrow{k_5'} \text{Products} \quad \text{(v)}$$

Scheme-2

Scheme 2 leads to the rate law as follows:

$$Rate = -\frac{d[BAB]}{dt} = k_4'[X][S] \quad (15)$$

Total effective concentration of BAB for scheme 2 was given by the equation (16)

$$[BAB]_t = [PhSO_2N^+H_2Br] + [PhSO_2NHBr] + HOBr + X \quad (16)$$

From equilibria (i), (ii), and (iii) in scheme 2

$$[PhSO_2N^+H_2Br] = \frac{[X][PhSO_2NH_2][H^+]}{K_1'K_2'K_3'[Ru(III)]} \quad (17)$$

$$[PhSO_2NHBr] = \frac{[X][PhSO_2NH_2]}{K_2'K_3'[Ru(III)]} \quad (18)$$

$$[HOBr] = \frac{[X]}{K_3'[Ru(III)]} \quad (19)$$

By solving for $[BAB]_t$ of equation (15) and equations (16), (17), (18) and (19) one gets

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

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

Substituting [X] in the rate equation (15) leads to the rate law equation

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

This rate law equation (22) is in agreement with the experimental observations, including a first-order in [BAB], an inverse fractional order in $[H^+]$, and [BSA] and a fractional order in [Ru(III)].

The energy of activation for ruthenium catalyzed reactions is less than uncatalyzed reaction indicating the rate of reaction for ruthenium catalyzed reaction is faster than uncatalyzed reactions. 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 and scheme 2. The high negative value of entropy of activation ($\Delta S^{\neq}$) indicates the formation of a rigid transition state by associative process.

Table-3
Temperature dependence and activation parameters for the reaction of Niacin with Bromamine-B [NA] = 2.0×10^{-2}mol dm^{-3} ;[BAB] = 2.0×10^{-4} mol dm^{-3}; [Ru (III)] = 6.215×10^{-6} mol dm^{-3} ; [HCl] =2.5×10^{-4} mol dm^{-3} ;Temp = 303 K;μ = 0.2 mol dm^{-3}

Temparature in K	k′ x 10^4 sec^{-1}	Thermodynamic parameters
298	4.60 (0.354)	Ea = 46. 424 (48 .053) kJ mol^{-1}
303	6.06 (0.558)	$\Delta S^{\neq}$ = – 161. 87 (– 177. 21) JK^{-1} mol^{-1}
308	8.70 (0.725)	$\Delta H^{\neq}$ = 43. 862 (45. 49) kJ mol^{-1}
313	11.51(0.932)	$\Delta G^{\neq}$ = 94. 560 (100. 07) kJ mol^{-1}
318	14.50 (1.258)	---

*The values in the parenthesis are for the uncatalyzed oxidation of niacin by BAB in HCl medium.

Conclusion

The oxidation of vitamin- B_3 was carried out by bromamine-B as oxidant. The ruthenium catalyzed reaction is very much faster than uncatalyzed reaction. The kinetic study of these reactions helpful for understanding mechanistic reactions of vitamin-B_3 in biochemical reactions.

Acknowledgement

One of the authors Chandrashekar acknowledges the Management of PES college of Engineering Mandya, for permission and encouragement.

References

1. Mahadevappa D.S., Ananda S., Murthy A.S.A. and Rangappa K.S., *Tetrahedron,* **10,** 1673 **(1984)**

2. Rao P.V.S., Subbaiah K.V. and Murthy P.S.N., *React Kinet,* Catol, Lett., **10,** 79, (**1979**) 11, 287 (**1979)**

3. Venkatesha B.M., Ananda S. and Mahadevappa D.S., *Indian J. Chem*., **30A,** 789-792 **(1991)**

4. Ananda S., Venkatesha B.M., Mahadevappa D.S. and Madegowda N.M., *Int J. Chem Kinet.,* **25,** 755-770 **(1993)**

5. Capella-Peiro E., Monferrer-ponsL., Garca-Alvarez-Coque C. and Esteve-Romeroj, *Analytical chimica Acta,* **427,** 193-100 **(2001)**

6. Khan Seemab, Rai M.K., Gupta U.K. and Rai J.K., *Indian Journal of chemistry*, **44A,** 98-101 (**2005**)

7. Wei Wang, Alice Basinger, Richard A. Neese, Barryshane, Su-A Myong, Mark Christiansen and Marc K Hellerstein., *Am.J. Physiol Endocrinal, metab,* **280(3)** E 540-547 **(2001)**

8. Ronald B. Goldberg and Terry A. Jacobson, *Mayoclin Proc.,* **83(4),** 470- 478 **(2008)**

9. Wei Wang, Alice Basinger, Richard A Neese, Mark Christiansen and Marc K., Heller stein, *Am.J. P. Physiol. Endocrinal. Metab,* **279(1),** E 50 **(2000)**

10. Dayalan A. and R. Vijayaraghvan V., *Indian J. Chem*, **40A,** 959 **(2001)**

11. Bundareva V.M., Ovchinnikava E.V. and rushkevich T.V., *React Kinet and Cat Lett***, 94(2),** 327-335 **(2008)**

12. Sonawane Vilas Y., *Res.J. Chem. Sci.,* **1(1),** 25-30 **(2011)**

13. Medjor O.W., Egharevba F., Akpoveta O.V., Ize-Iyamu O.K. and Jatto E.O., *Res. J. Chem. Sci.,* **2(1),** 38-44 **(2012)**

14. Atohoun Y.G.S., Kuevi U.A., Kpota A.H. and Mensah J.B., *Res.J. Chem. Sci.,* **1(8),** 18-23 **(2011)**

15. Ahmed M.S. and Mahadevappa D.S., Talanta, **27,** 669 **(1980)**

16. Furniss B.S., Hannatord A.J., Smith P.W.G. and Tatchell A.R., Vogels Text book of organic chemistry, Pearson Publication, **1213 (2009)**

17. Pryde B.G. and Soper F.G., *J. Chem., Soc,* **1582** (**1926**) **1514** (**1931**)

18. Morris J.C., Salazar J.A. and Wineman M.A., *J. Ame, Chem soc*., **70,** 2036 **(1948)**

19. Bishop E. and Jennings V.J., *Talanta*, **1,** 197 **(1958)**

20. Narayanan S.S., and Rao V.R.S., *Radiochem, Acta,* **32,** 211 **(1983)**

21. Subhashini M., Subramanian M. and Rao V.R.S., *Talanta*, **32,** 1082 **(1985)**

22. Cady H.H. and Connick R.E., *J Am chem. Soc,* **80,** 2646 **(1958)**

23. Connick R.E. and Fine D.A., *J Am chem. Soc,* **82,** 4187 **(1960)**

24. Davtokratova T., Analytical chemistry of ruthenium, Academy of Sciences, USSR, **54**,71, 97 **(1963)**

25. Griffith W.P., The chemistry of the rare platinum metals, (Interscience publishers), 141 **(1967)**

26. Backhours J.R., Doyer F.D. and Shales N., *Proc. Rov soc*, **83,** 146 **(1950)**

27. Singh B. Singh N.B. and Saxena B.B.L., *J. Indian Chemical Soc.,* **61**, 319 **(1984)**

28. Singh B., Singh P.K. and Singh D., *J. mol. Cat*, **78**, 207 **(1988)**

29. Ananda S., Venkatesha B.M., Mahadevappa D.S. and Madegowda N.M., *Int J. Chem Kinet* **25,** 755 **(1993)**