International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol. 3, No.3, pp 1096-1101, July-Sept 2011

Mechanistic study of oxidation of alcohols by N-bromoisonicotinamide in aqueous acetic acid medium

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Abstract: Kinetics of oxidation of alcohols viz. methanol, ethanol, propanol, butanol, isobutanol, pentanol, isopentanol and hexanol, have been investigated at 328 K, by a newly developed oxidant N-bromoisonicotinamide (NBIN) in aqueous acetic acid medium. The reaction is first order in [NBIN], zero order in [substrate] and inverse fractional order in $[H^+]$. Increase in ionic strength increases the rate and addition of the reaction product isonicotinamide has a slight retarding effect on the reaction rate. Increase in the dielectric constant of the medium increases the rate. Activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperatures and oxidation products are identified. A most probable reaction mechanism is proposed and an appropriate rate law is deduced to account for the observed kinetic data.

Keywords: kinetics, oxidation, alcohols, N-bromoisonicotinamide.

Introduction:

N-halo compounds are known to be versatile oxidizing agents[1]. They are being used in kinetics, analytical[2], organic structural investigations and in synthesizing organic substrates[3]. N-halo compounds are referred to as positive halogen compounds. The kinetics of oxidation of alcohols by N-bromo succinimde[4,5], N-chlorosuccinimide[6], N-bromo acetamide[7], Bromamine-T[8], N-chloronicotinamide[9], Chloraamine-T[10], N-bromophthalimide[11], 1-Chloro - benzotriazole[12] is already known. The kinetics of oxidation of amino acids by N-bromonicotinamide[13]is already reported. N-bromoisonicotinamide[14] (NBIN) is a new, mild, stable, effective and efficient oxidant for organic substrates. NBIN is a biologically important oxidizing agent, due to its reported antimicrobial activity by disc diffusion method[15] against *Staphylococcus aureus, Kiebsiella agerogenoes, Proteus vulgaris, Salmonella typhi, Candida alebicans,* and *Aspergillus niger* at different concentrations. However, the kinetics of oxidation of alcohols by NBIN in aqueous acetic acid medium is not reported so far and hence need for the title investigation.

Experimental:

NBIN was prepared[16] in acetic acid (Merck) and the purity was checked iodometrically. All the other chemicals were of AnalaR grade. The alcohols were prepared in acetic acid. Kinetics runs were carried out under pseudo-first order conditions ([alcohols] >> [NBIN]). Requisite amounts of alcohols, perchloric acid sodium sulphate and aqueous acetic acid were taken in a jena glass reaction vessel and placed in a water thermostat maintained at the desired temperature for 30 min. The reaction was initiated by a rapid addition of NBIN solution and progress was followed by estimating iodometrically the amount of unconsumed NBIN at regular intervals of time.

Result and discussion:

The kinetics and oxidation of alcohols by NBIN was investigated at several initial concentrations of the reactants. Under pseudo-first order conditions [alcohols] >> [NBIN], the oxidation proceeds smoothly at 55 ^{0}C in aqueous acetic acid medium. The plot of log [NBIN] against time is found to be linear with a linear with a correlation coefficient >0.999, showing a first order dependence on [NBIN].

The constancy of pseudo-first order rate constants at different [substrate] at constant [NBIN], indicates that the reaction is zero-order in [alcohols] (Table-1). Effect of [H^+] is investigated by varying [$HClO_4$] and by keeping the other parameters constant. Increase in [H^+] ions decreased the rate constant of the reaction (Table-1). The plot of log k_{obs} versus log [H^+] is linear with negative slope (-0.36), indicating inverse fractional-order dependence on [$HClO_4$]. Effect of [Br^-] on the rate of the reaction has also been studied by increasing [KBr] at constant [H^+]. Addition of KBr has no significant effect on the reaction.

In order to determine the rate dependence on solvent composition, kinetics is followed in glacial acetic acid-water mixtures, in which ratio of water to acetic acid is varied. It is observed that an increase in the dielectric constant of the medium increases the rate constant (Table-1). The plot log k_{obs} versus 1/D is linear with a positive slope.

The reaction is conducted at different ionic strengths using Na_2SO_4 and keeping the concentration of other reactants constant. Increasing the ionic strength of the medium increases the rate (Table-1). The plot of log k_{obs} vs μ is linear (r=0.989) with positive slope, which indicates that the reaction is between two dipoles.

The oxidation of alcohols has been studied at different temperatures (318-333 K). The results are shown in (Table-2). The Arrhenius plot log k_{obs} versus 1/T is linear (r=0.999). From the plot, the Arrhenius and thermodynamic activation parameters are evaluated.

Table-1: Effect of [substrate], [NBIN], CH_3COOH-H_2O %, [$HClO_4$], [Na_2SO_4] and the rate constants for the oxidation of methanol by NBIN at 328 K.

[Methanol] x 10^2 M	[NBIN] x 10^3 M	CH_3COOH-H_2O % (v/v)	[$HClO_4$] x 10 M	[Na_2SO_4] x 10 M	k_{obs} x 10^4 (s^{-1})
3.0	3.0	70-30	1.0	--	6.87
4.0	3.0	70-30	1.0	--	6.91
5.0	3.0	70-30	1.0	--	6.91
6.0	3.0	70-30	1.0	--	6.91
7.0	3.0	70-30	1.0	--	6.83
4.0	3.0	70-30	1.0	--	6.91
4.0	4.0	70-30	1.0	--	7.12
4.0	5.0	70-30	1.0	--	6.87
4.0	6.0	70-30	1.0	--	6.86
4.0	7.0	70-30	1.0	--	7.10
4.0	3.0	70-30	0.2	--	12.7
4.0	3.0	70-30	0.4	--	10.3
4.0	3.0	70-30	0.6	--	8.98
4.0	3.0	70-30	0.8	--	7.87
4.0	3.0	70-30	1.0	--	6.91
4.0	3.0	70-30	1.0	0.25	9.14
4.0	3.0	70-30	1.0	0.50	14.9
4.0	3.0	70-30	1.0	0.75	21.9

4.0	3.0	70-30	1.0	1.00	26.7
4.0	3.0	70-30	1.0	1.25	31.8
4.0	3.0	60-40	1.0	--	9.23
4.0	3.0	70-30	1.0	--	6.91
4.0	3.0	80-20	1.0	--	4.59
4.0	3.0	90-10	1.0	--	2.13

Table-2: Rate constants for the oxidation of Alcohols by NIBN and Activation parameters:
[Alcohols] = 4.0×10^{-2} M, [NBIN] = 3.0×10^{-3} M, [$HClO_4$] = 1.0×10^{-1} M,
Solvent (v/v) = 70% CH_3COOH -30% H_2O.

Substrate	$k_{obs}\times10^4$ (s^{-1})				Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
	318K	323K	328K	333K				
Methanol	3.71	5.45	6.91	10.96	63.57	60.84	-52.36	43.66
Ethanol	3.72	5.16	7.18	11.21	63.58	60.86	-52.26	43.71
Propanol	3.74	5.41	6.97	11.09	63.62	60.89	-52.32	43.73
Butanol	3.45	5.29	6.88	11.07	64.39	61.66	-51.22	44.87
Iso-butanol	3.62	5.49	7.14	10.97	61.27	60.55	-50.35	44.03
Pentanol	3.48	5.39	6.91	10.76	65.85	63.15	-50.88	46.44
Iso-pentanol	3.62	5.61	7.11	10.99	64.67	61.94	-51.24	44.67
Hexanol	3.58	5.46	6.98	10.89	65.03	62.30	-50.47	45.75

Mechanism:

Under the experimental conditions, the possible oxidizing species are Br_2, HOBr, H_2OBr^+, and $NBINH^+$ in aqueous solution. The reaction is first order in [NBIN] and the addition of isonicotinamide has a slight retarding effect on the rate. Both these factors indicate that HOBr may be the reactive species. It has been reported earlier[17] in the case of N-halo oxidants that, in the absence of mineral acids, HOBr is the reactive oxidant species. Since there is no effect due to [KBr], the possibility of the involvement of Br_2 is also ruled out.

The rate of the reaction decreases with the increase in [H^+]. This may be explained by assuming equilibrium between unprotonated and protonated oxidant[18].

$$NBIN + H^+ \leftrightarrows NBINH^+$$

The unprotonated species is involved in the formation of the active oxidant.

$$NBINH^+ \overset{K}{\rightleftarrows} NBIN + H^+ \qquad \text{------ (1)}$$

$$\text{NBIN} + H_2O \underset{\text{slow}}{\overset{k_2}{\rightleftharpoons}} \text{HOBr} + \text{Isonicotinamide} \qquad \text{------ (2)}$$

$$\text{HOBr} + \text{Substrate} \xrightarrow[\text{fast}]{} \text{Complex} \qquad \text{-- ---- (3)}$$

$$\text{Complex} \longrightarrow \text{Products} \qquad \text{------- (4)}$$

$$\text{Rate} = k_2\,[\text{NBIN}]\,[H_2O] \qquad \text{------- (5)}$$

Applying equilibrium approximation to step (1)

$$K = \frac{[\text{NBIN}]\,[H^+]}{[\text{NBINH}^+]} \qquad \text{------ (6)}$$

$$K\,[\text{NBINH}^+] = [\text{NBIN}]\,[H^+] \qquad \text{------- (7)}$$

$$[\text{NBIN}]_e = \frac{K\,[\text{NBINH}^+]}{[H^+]} \qquad \text{------- (8)}$$

Where $[\text{NBIN}]_e$ is the concentration of NBIN at equilibrium

Substituting $[\text{NBIN}]_e$ in rate equation

$$\text{Rate} = \frac{k_2\,K\,[\text{NBINH}^+]\,[H_2O]}{[H^+]} \qquad \text{------- (9)}$$

The total effective concentration of NBIN is $[\text{NBIN}]_t$

$$[\text{NBIN}]_t = [\text{NBIN}]_e + [\text{NBINH}^+] \qquad \text{------- (10)}$$

$$[\text{NBIN}]_t = \frac{K\,[\text{NBINH}^+]}{[H^+]} + [\text{NBINH}^+] \qquad \text{------- (11)}$$

$$[\text{NBIN}]_t = [\text{NBINH}^+] \left[\frac{K}{[H^+]} + 1 \right] \qquad \text{------- (12)}$$

$$[\text{NBINH}^+] = \frac{[\text{NBIN}]_t}{(K/[H^+]) + 1} \qquad \text{------- (13)}$$

Substituting for $[\text{NBINH}^+]$ in rate equation

$$\text{Rate} = k_2\,K\,[H_2O] / [H^+] \;\; x \;\; \frac{[\text{NBIN}]_t}{(K/[H^+]) + 1} \qquad \text{------- (14)}$$

$$\text{Rate} = k_2\, K\, [H_2O] / [H^+] \text{ x } \frac{[\text{NBIN}]_t}{\{(K + [H^+]) / [H^+]\}} \qquad \text{-------} (15)$$

$$\text{Rate} = \frac{k_2\, K\, [H_2O]\, [\text{NBIN}]_t}{(K + [H^+])} \qquad \text{-------} (16)$$

$$\text{Rate} = \frac{k\, [\text{NBIN}]_t}{(K + [H^+])} \qquad \text{where as, } k = k_2\, K\, [H_2O] \qquad \text{-------} (17)$$

The above equation can be written as follows:

$$\frac{1}{k'} = \frac{K + [H^+]}{k\, [\text{NBIN}]_t} \qquad \text{-------} (18)$$

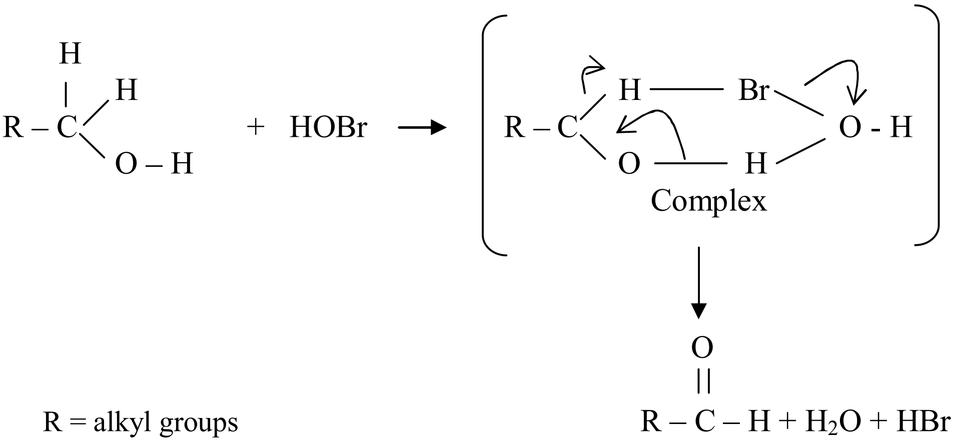
$$\frac{1}{k'} = \frac{K}{k\, [\text{NBIN}]_t} + \frac{[H^+]}{k\, [\text{NBIN}]_t} \qquad \text{-------} (19)$$

When $1/k'$ is plotted against $[H^+]$, a straight line is obtained. The slope of the line is $1/k[\text{NBIN}]_t$. From the value of intercept and substituting the value of $k[\text{NBIN}]_t$, the equilibrium constant K is calculated. Since $K < [H^+]$ (0.1), equation 17 takes the form,

$$\text{Rate} = \frac{k\, [\text{NBIN}]_t}{[H^+]}$$

The rate law shows that the reaction follows first order kinetics with respect to [NBIN] and inverse fractional order kinetics with respect to $[H^+]$.

The structure of the complex and the formation of products from it are given as follows:



R = alkyl groups

A similar complex is given the study of oxidation kinetics of aliphatic alcohols[9] by NCN. The increase of rate with increase in the ionic strength[19] and dielectric constant of the medium explain the reaction between two dipoles in the rate determining step, which is in agreement with Kirkwood theory[20]. The high positive values of free energy of activation and the enthalpy of activation indicate that the transition state is highly solvated, whereas the negative value of entropy of activation indicates that the activated complex is cyclic in nature[21,22].

Stoichiometric study and product analysis:

The reaction mixture containing excess of NBIN over alcohols in the presence of $HClO_4$ and Na_2SO_4 was kept at the room temperature for 36 h. Estimation of unreacted NBIN showed that one mole alcohols reacted with one mole of NBIN. The overall stoichiometry (1:1) of the oxidation reaction may be represented as

$$ROH + C_5H_4NCONHBr \rightarrow RCHO + INA + RBr$$

R = alkyl groups, INA =isonicotinamide

The corresponding aldehyde was found to be the major product of oxidation, which was confirmed by IR spectra which show bands at 3440 cm^{-1} and 1720 cm^{-1} for O-H stretching and C=O stretching. Formation of benzaldehyde was also confirmed by the addition of 2,4 dinitro phenyl hydrazine. The aldehyde was converted to 2,4 dinitrophenyl hydrazone. The melting point of 2,4-DNP derivative is 253°C (lit. m.p. 248°C). The product was also confirmed by thin layer chromatography.

References

1. Filler R., Chem. Rev., 1963, 63, 21.
2. Foster R.,"Organic Charge Transfer Complexes", Academic Press, New York, 1969.
3. Fieser M. and Fieser L.F., "Reagents for Organic Synthesis", Wiley Interscience, New York, 1967.
4. Thigarajan V. and Venkatasubramanium N. , Indian J. Chem., 1970, 8, 809.
5. Gopalakrishnan G. and Pai B.R. , Indian J. Chem., 1979, 18, 92.
6. Srinivasan N.S. and Venkatasubramanium V. , Tetrahedron Lett., 1973, 30, 419.
7. Negi S.C. and Benerji K.K , Indian J. Chem., Sec.B., 1982, 21, 846.
8. Bharat singh A.K. and Saxena B.L. , Tetrahedron Letts., 1984, 40, 5203.
9. Mathiyalagan N., Sridharan, R. and Priya V., J. Indian Chem. Soc., 2005, 82, 795.
10. Naidu H M K and Mahadevappa D.S., Indian J. Chem., 1988, 27, 880.
11. Jagdish bharad and Milind ubale., J Indian Chem. Soc., 2009, 86, 481.
12. Hiremath R. and Mayanna M.S., J Chem. Sci., 2005, 177, 333.
13. Vivekanandan K., J. Indian Chem. Soc., 2008, 85, 1027.
14. Mathiyalagan N. and Balasubramaniyan M., Oriental J. Chem., 2010, 26, 1541.
15. NCCLS., performance standards for Antimicrobial Disc test, 5th ed., Approved Standard., National Committee for Clinical Laboratory standards, M2-M5, PA., 1993.
16. Mathur N K and Narang C K , "The Determination of Organic Compounds with N-Bromosuccinimide"., Academic Press, New York, 1975.
17. Venkateswaralu S. and Jagannadhan V., Indian J. Chem., 1988, 27A, 314.
18. Mythili C K. and Rangappa K S., Indian J. Chem., 1990, 29A, 676.
19. Mathiyalagan N. and Sridharan R., J. Indian Chem. Soc., 2006, 83, 434.
20. Kirkwood K G., J. Chem. Phys., 1934, 2, 351.
21. Vivekanandan K. and Nambi K., J. Indian Chem. Soc., 1999, 76, 198.
22. Bharagava K. and Sethuram B. Rao T K., Indian J. Chem., 1978, 16, 651.

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