Asian Journal of Chemistry Vol. 22, No. 1 (2010), 265-270

Kinetics and Mechanism of Oxidation of Aliphatic Alcohols by N-Bromonicotinamide in Aqueous Acetic Acid

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Kinetics of oxidation of four aliphatic alcohols by N-bromonicotinamide (NBN) in 60 % aqueous acetic acid has been investigated. The reaction follows first order kinetics with respect to both [NBN] and [Substrate]. A increase in the dielectric constant increases the rate. Addition of nicotinamide has a negligible effect on the rate of oxidation. The product of oxidation is the corresponding aldehyde and ketone. From the effect of temperature on the reaction rate the Arrhenius and activation parameters have been calculated. A suitable mechanism has been proposed and rate law explaining the experimental results is derived.

Key Words: Kinetics, Oxidation, N-Bromonicotinamide, Aliphatic alcohols.

INTRODUCTION

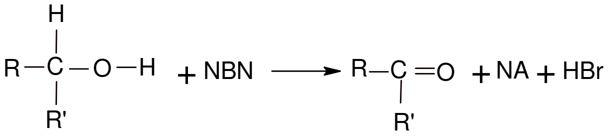
N-Halogeno compounds having N-X bonds are known to be versatile oxidizing agents[1]. Literature survey reveals that the kinetics of oxidation of alcohols has been reported using various N-halo compounds[2]. But there is no oxidation studies available pertaining to the oxidation of alcohols with the newly developed oxidant N-bromonicotinamide (NBN)[3]. The antibacterial activity of NBN against *E. coli, Solmonella enterocolitica, Shigella flexeri* and *Staphycoccus aures* at different concentrations by disc diffusion method has been reported[3]. The biological importance of nicotinamide, a derivative of B_2 vitamin nicotinic acid has been shown to prevent both chemically induced and spontaneous development of diabetes mellitus in animal models of type 1 (insulin independent) diabetes. It enhances β-cell regeneration in partially pancreatictomized rats[4]. Herein, the results of kinetics of oxidation of four aliphatic alcohols with N-bromonicotinamide (NBN) in aqueous acetic acid medium by titrimetric method with a view to probe the mechanism of oxidation are reported.

EXPERIMENTAL

Doubly distilled conductivity water was used throughout the study. The alcohols (AR) were used as such without further purification. Acetic acid (AR, Qualigens) purified by standard method. Standard solution of N-bromonicotinamide (NBN) was prepared[5] in acetic acid and its purity was checked iodometrically[6]. Perchloric acid (AR) was used as a source of $[H^+]$.

The reaction was carried out under pseudo first order condition ([alcohol] >> [NBN]). The reaction was followed iodometrically by quenching aliquots samples in an excess of KI (*ca.* 10 %) in sulphuric acid (*ca.* 1 M). The liberated iodine was titrated against thiosulphate solution using starch indicator.

Stoichiometry and product analysis: The reaction mixture containing excess of N-bromonicotinamide over alcohol (3:1) in the presence of $HClO_4$ and $NaClO_4$ were kept at the room temperature for 36 h. Estimation of unreacted N-bromonicotinamide showed that one mole of alcohol reacted with one mole of N-bromonicotinamide. The overall stoichiometry of the oxidation reaction may be represented as:



$$R-\overset{\displaystyle H}{\underset{\displaystyle R'}{C}}-O-H + NBN \longrightarrow R-\underset{\displaystyle R'}{C}=O + NA + HBr$$

NA = Nicotinamide, R = CH_3 or C_2H_5 or C_3H_7, R′ = H or CH_3 group

Product study was made keeping concentration of N-bromonicotinamide in excess over alcohol. The reaction was allowed to proceed to completion by keeping it in a thermostat at 40 ºC for 4 h. The excess oxidant was decomposed by 2 N sulphuric acid, potassium iodide and sodium thiosulphate solution. The solution was then shaken well with ether. The ethereal layer was washed with water several times and kept on a water bath for ether evaporation and cooled to get the product. The product aldehydes or ketones were identified by IR spectrum and the melting point of the 2,4-dinitrophenyl hydrazine derivatives of the products.

RESULTS AND DISCUSSION

Under the condition [NBN] << [alcohol] the plot of log (a-x) *versus* time is linear (r = 0.9983) indicating first order dependence of rate on [NBN]. The rate constant is reproducible upto 3 %. The pseudo first order rate constant doesn't change with increase in initial concentration of the oxidant.

Increase in [alcohol] has a positive effect on the rate. A plot of log [alcohol] *versus* log k_1 is linear with slope unity, indicating first order dependence of rate on [alcohol] (Table-1). The effect of $[H^+]$ is investigated by varying $[HClO_4]$ at constant Br^- (Table-2). The effect of Br^- is carried out by varying KBr at constant $[H^+]$. The rate is found to be not affected by $[H^+]$ or $[Br^-]$.The rate constant increases on increasing the dielectric constant of the medium (Table-3)[7]. The increase in concentration of nicotinamide (NA) has negligible effect on rate of the reaction. Addition of salts like $NaClO_4$ to the reaction medium has no effect on the rate. The reaction mixture failed to initiate polymerization of aqueous acryl amide solution showing the absence of free radicals. The oxidation of all the four alcohols is studied at different temperatures (313-328 K), keeping the other experimental conditions constant. The Arrhenius plot of log k_2 *versus* 1/T is linear (r = 0.971). The Arrhenius and activation parameters are evaluated (Table-4).

TABLE-1
EFFECT OF VARIATION OF [ALCOHOL] AND [NBN] ON REACTION RATE AT 313 K
[$HClO_4$] = 0.1 M; [$NaClO_4$] = 0.1 M; Solvent = 60 % Acetic acid (v/v)

[Alcohol] 10^2 M	[NBN] 10^3 M	$k_1 \times 10^4$ s^{-1}			
		Propan-1-ol	Butan-1-ol	Propan-2-ol	Butan-2-ol
1	2	0.69	1.38	3.90	4.60
2	2	1.15	2.60	4.60	8.67
3	2	2.30	3.92	6.90	13.06
4	2	4.60	5.02	9.12	16.30
1	1	0.60	1.39	3.87	4.62
1	2	0.69	1.38	3.90	4.60
1	3	0.70	1.25	3.88	4.59
1	4	0.69	1.32	3.90	4.60

TABLE-2
EFFECT OF VARIATION OF [$HClO_4$] ON REACTION RATE AT 313 K
[Alcohol] = 1×10^{-2} M; [NBN] = 2×10^{-3} M; Solvent = 60 % Acetic acid (v/v); [$NaClO_4$] =0.1 M

[$HClO_4$] × 10 M	$k_1 \times 10^4$ s^{-1}			
	Propan-1-ol	Butan-1-ol	Propan-2-ol	Butan-2-ol
1	0.69	1.38	3.90	4.60
2	0.65	1.43	3.89	4.59
3	0.67	1.42	3.86	4.61
4	0.68	1.41	3.88	4.60

TABLE-3
EFFECT OF VARIATION OF SOLVENT POLARITY ON REACTION RATE AT 313 K
[Alcohol] = 1×10^{-2} M; [$HClO_4$] = 0.1 M; [NBN] = 2×10^{-3} M; [$NaClO_4$] = 0.1 M

Percentage of acetic acid	$k_1 \times 10^4$ s^{-1}			
	Propan-1-ol	Butan-1-ol	Propan-2-ol	Butan-2-ol
40	1.24	2.56	4.83	6.84
50	0.91	1.95	4.31	5.30
60	0.69	1.38	3.90	4.60
70	0.46	0.76	3.23	3.14

TABLE-4
ARRHENIUS AND THERMODYNAMIC PARAMETERS FOR
THE OXIDATION OF VARIOUS ALCOHOLS BY NBN
[Alcohol] = 1×10^{-2} M; [$HClO_4$] = 0.1 M; [NBN] = 2×10^{-3} M; [$NaClO_4$] = 0.1 M;
Solvent = 60 % Acetic acid (v/v)

Substrate	$k_2 \times 10^2$ s^{-1}				E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	log A
	313 K	318 K	323 K	328 K					
Propan-1-ol	0.69	0.99	1.40	2.78	24.13	21.53	-217.89	89.73	7.11
Butan-1-ol	1.38	1.60	2.70	5.10	23.67	21.07	-213.62	87.93	7.24
Propan-2-ol	3.90	6.00	9.50	14.30	23.28	20.68	-206.19	85.22	7.54
Butan-2-ol	4.60	7.80	12.10	16.90	23.24	20.64	-204.98	84.79	7.59

Order of reactivity and iso-kinetic relationship: The order of reactivity is butane-2-ol > propane-2-ol > butane-1-ol > propane-1-ol. It is seen from the Table-4 that the activation energy is highest for slowest reaction. Such a reactivity order has been reported earlier in the oxidation of aliphatic alcohols by bromate[8] and N-chloronicotinamide[9].

The rates of oxidation of the four aliphatic alcohols correlate well with Taft's σ^* substituents constants[10] with negative value reaction constants. The values of ρ^* at 318, 323 and 328 K are -0.097 (r = 0.9951), -0.093 (r = 0.9764) and -0.089 (r = 0.971), respectively.

Exner plot: Exner[11] suggested the validity of such a linear correlation between log k_2 at 323 K *versus* log k_2 at 313 K.

$$\log k_2 (T_2) = a + b \log k_2 (T_1)$$

where $T_2 > T_1$.

Thus satisfactory correlation coefficient (r = 0.9973) is obtained for a plot of log k_2 (50 ºC) *versus* log k_2 (40 ºC) which was linear (slope = 0.888). This serves as an argument that all the four alcohols follow a common mechanism. From the slope of the Exner plot the isokinetic temperature (β) is calculated using the following equation[12]:

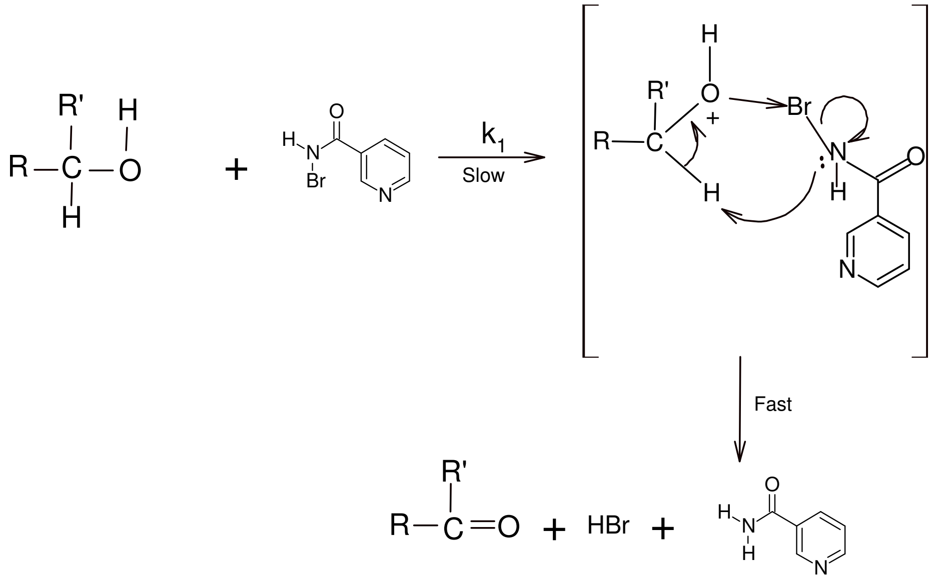
$$\beta = \frac{T_1 T_2 (b-1)}{b(T_2 - T_1)}$$

The slope (b) is less than one and β (432 K) is greater than T_1. These results indicate a decreasing selectivity with the increase in temperature and the reaction series is characterized by compensation effect between $\Delta H^\#$ and $\Delta S^\#$.

Mechanism: Under the experimental conditions studied, the possible oxidizing species are Br_2, HOBr, H_2OBr^+, $NBNH^+$ and NBN in aqueous solution. Since there was no effect due to H^+ and Br^- the possibilities of involvement of Br_2, HOBr, H_2OBr^+ and $NBNH^+$ are ruled out. Hence NBN itself seems to be the oxidizing species in the oxidation of alcohols[13]. Deno and Potter[14] investigated the mechanism and synthetic utility of oxidative cleavage of ethers by aqueous bromine. A first order dependence both on [ether] and [bromine] has been reported. A suitable mechanism involving simultaneous loss of H^+ from carbon and an electron pair from ether oxygen has been proposed. Hence it is assumed that the NBN is the effective oxidising species in the present investigation and keeping the above data in consideration the following mechanism is proposed for the oxidation of four aliphatic alcohols by NBN. A similar mechanism has been reported by Thiagarajan and Venkatasubramanian[15] in the oxidation of secondary alcohols with NBS.

The rate-law predicts the first order dependence on NBN and alcohol. The addition H^+ and Cl^- have no effect on the rate of the reaction. Absence of ionic strength on rate precludes the involvement of two ions in the rate sequence. An increase in the percentage of acetic acid decreases the rate of reaction and log k_1 *vs.* 1/D is linear with negative slope indicating the dipole-dipole type of interaction.

The proposed mechanism[16] is well supported by the values of thermodynamic parameters and energy of activation (Table-4). The high positive values of free energy of activation ($\Delta G^{\#}$) and the enthalpy of activation ($\Delta H^{\#}$) indicate that transition state is highly solvated, whereas the negative value entropy of activation ($\Delta S^{\#}$) indicates that the activated complex is cyclic nature[6,17]. The activation enthalpies and entropies of oxidation of all the four aliphatic alcohols are linearly related (r = 0.9973) implying that all the four alcohols undergo oxidation by the same mechanism.



$\text{Rate} = k_1[\text{Alcohol}][\text{NBN}]$

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(*Received*: 23 December 2008; *Accepted*: 5 September 2009) AJC-7831