Study of Reaction Rates and Pathways for the Oxidation of Hydroxyamine by N-halocompound under Alkaline Condition

Shalini Bajpai
Chemistry Department, D.B.S.P.G. College, Kanpur, India

Abstract
The systematic kinetic results were reported for the oxidation of three hydroxyamine viz; 2-hydroxyethylamine, bis(2-hydroxyethyl)amine, tris-(2-hydroxyethyl)amine by alkaline N-halocompound. The reaction exhibits first-order dependence on N-halocompound. However, the reaction order with respect to hydroxyamines and $[OH^-]$ decreases from unity to zero at higher concentration of hydroxyamine and $[OH^-]$, respectively. The reaction rate is enhanced by succinimide at low concentration but becomes independent of succinimide at higher concentration. A reaction mechanism consistent with the observed kinetic behavior is proposed.
Keywords: *Oxidation, kinetics, hydroxyamine, N-halocompound.*

I. Introduction

N-halocompounds i.e., N-bromosuccinimide (NBS) has been widely used in the quantitative determination of organic compounds. The functionality of NBS as an analytical reagent as well as oxidizing agent has been reviewed [1,2]. Most of the investigations of NBS oxidation of organic substances have assumed that the molecular NBS acts only through its positive polar end producing Br^+ which is subsequently solvated. So, H_2O+Br^+ has been recommended as the effective oxidising species of NBS in acidic medium. In acidic medium the protonated form of NBS i.e., N^+BSH revealed as reactive species of NBS in presence of mercuric acetate. Thus, it is considered that NBS is a source of positive halogen and exploited as an oxidant for a variety of substances in both acidic and alkaline medium [3-9]. However, there are only few reports on the oxidation reactions of NBS in alkaline medium. The oxidation of hydroxylamine by NBS in aqueous acetic acid medium has been studied. In absence of catalyst, the order of reactions were first and zero in substrate and acid, respectively. While, in alkaline medium, the order of reaction in substrate and alkali was found to be decreased from unity to zero at higher concentrations of substrate and alkali, respectively. Therefore, the title reaction has been studied in detail and kinetic data are reported in the present communication.

II. Material and Method

The reagents employed were 2-hydroxyethylamine, bis-2(hydroxyethyl)amine, tris-2-hydroxyethylamine (AR grade), N-bromosuccinimide (Thomas Baker, AR), $NaClO_4$, Succinimide, NaOH (all Analar). All solutions were prepared in doubly distilled water. Solution of NBS was prepared fresh and standardized iodometrically.

A reaction mixture was made by adding a fixed amount of NBS solution to a mixture containing the hydroxyamine being tested (2-hydroxyethylamine, bis-2-hydroxyethylamine, tris-2-hydroxyethylamine) and NaOH. The total volume was made up to 50 ml using double-distilled water. The reaction was carried out at a constant temperature of 35°C. At different time intervals, samples were taken and leftover amount of NBS was measured by titrating against sodium thiosulphate. The rate of reaction was observed by measuring how much NBS was left reacted over time.

Stoichiometry and Product Analysis

By varying the ratio of hydroxyamine i.e., HEA, bHEA, and tHEA to NBS, were mixed for 72 h at 35°C in presence of sodium hydroxide. The unreacted amount of NBS was observed iodometrically. The results reveal that one mole of HEA, bHEA, and tHEA consumed one, two and three mole of NBS to give formaldehyde, ammonia and succinimide as the end product detected by spot test [10]. The presence of formaldehyde was further confirmed by converting it into 2,4-dinitrophenylhydrazone and comparing it with an authentic sample (M.P. and TLC).

III. Results and Discussion

The reaction between the hydroxyamines and NBS was studied at a constant temperature of 35°C. The effect of different concentrations of NBS was checked by while keeping the concentrations of other substances constant. The first order nature was confirmed by plotting graph of log[NBS] versus time. In order to determine the effect of substrate on the reaction rate, the plots of k_{obs} versus [substrate] deviated from the linearity at higher [substrate] while, the plots of $1/k_{obs}$ versus 1/[substrate] were linear with positive intercepts, suggesting a Michaelis-Menten type kinetics, which confirming that the order of reaction in [substrate] decreases from unity to zero at higher concentration of substrate [Table – I].

Table 1: Effect of [substrate] on the rate constant at 35°C.

10^2 [Substrate]	k_{obs} x 10^4 (s^{-1})		
	2-hydroxyethylamine (HEA) or (A)	bis-2-hydroxyethyl amine (bHEA) or (B)	tris-2-hydroxyethylamine (tHEA) or (C)
0.5	1.25	8.00	2.45
1.0	2.00	12.80	3.65
2.0	2.82	18.27	4.79
3.0	3.50	23.00	5.75
4.0	4.10	25.00	6.25

[NBS]=2.0×10^{-3} mol dm^3]; [OH$^-$] = 1.0×10^{-2} mol dm^{-3}.

To study the effect of alkali on the rate of reaction, the oxidation of hydroxyamine was studied at various initial concentrations of NaOH and at a fixed ionic strength, the k_{obs} increases and a plot of $[k_{obs}]^{-1}$ versus $[OH^-]^{-1}$ was found to be linear with an intercept shows that the order of reaction in $[OH^-]$ decreases from unity to zero at higher concentrations of NaOH [Table-2].

Table–2: Effect of [OH$^-$] on the rate constant at 35°C

$10^2[OH^-]$	$k_{obs} \times 10^4$ (s^{-1})		
	2-hydroxyethylamine (A)	bis-2(hydroxyethyl)amine (B)	tris-(2-hydroxyethyl)amine (C)
0.5	1.40	9.10	2.30
1.0	2.82	18.27	4.79
2.0	4.35	25.21	6.90
3.0	6.40	29.00	9.00
4.0	8.00	31.25	10.25

[NBS] = 2.0×10^{-3} moldm^{-3} ; [S] = 2.0×10^{-2} moldm^{-3}

In order to observe the effect of succinimide (reaction product of NBS) in the reaction mixture the observed rate constants evaluated from the slope of linear plots, e.g. the observed rate constant evaluate from the slop of linear plots, eg. the observed rate constants were 4.79, 5·11, 8.31 6.64, 8.31, 9.03,10.23, 10.40 x 10^{-4} in the presence of nil, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 x10^{-3} mol dm^{-3} succinimide, respectively at 35°C in the presence of constant concentration of NBS, substrate and OH$^-$ in case case of tHEA. It is apparent that k_{obs} increases on increasing [succinimide] up to 6.0x10^{-3} moldm^{-3}. However, a further increase in [succinimide] had a negligible effect on k_{obs}. A plot of [succinimide]/k_{obs} Versus [succinimide] was linear with an intercept at lower [succinimide] i.e. up to 6.0X10^{-3} moldm^{-3} (Fig.1)

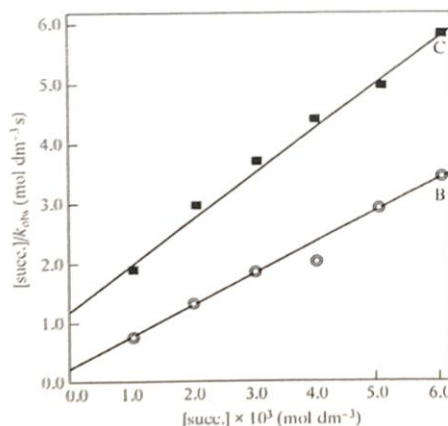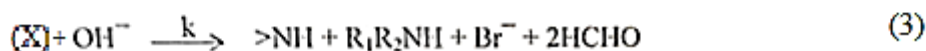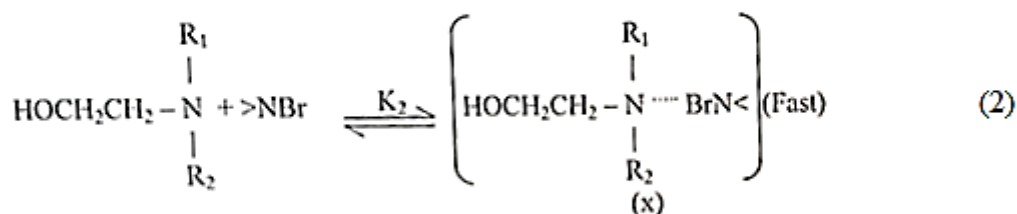Fig. 1. Plots of [succ]/k_{obs} versus [succ.] at 35°C

Addition of sodium perchlorate (up to 2×10^{-2} mol dm^{-3}) to the reaction mixture had no effect on the observed rate constant. The reaction were also studied at different temperatures, viz.. 35, 40, 45 and 50°C and the thermodynamic parameters evaluated [Table-3]

Table-3: Thermodynamic parameters for oxidation of hydroxy amines.

Thermodynamic parameters	2-hydroxyethylamine (A)	bis-2 (hydroxyethyl)amine (B)	tris-2 (hydroxyethyl) amine (C)
ΔE(kJ mol^{-1})	62.79	68.59	59.80
log A	7.20	8.78	6.40
$\Delta H^{\#}$(kJ mol^{-1})	61.14	65.90	55.12
$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	106.80	76.20	119.50
$\Delta G^{\#}$ (kJ mol^{-1})	95.00	91.70	92.80

In alkaline medium and in the absence of catalyst. OBr⁻ has been considered as reactive species of NBS according to following equilibria:

$$>NBr + OH^- \underset{}{\overset{k_{obs}}{\rightleftharpoons}} OBr^- + >NH \qquad \ldots\ldots\ldots\ldots..(1)$$
(NBS)   (Succ.)

If OBr⁻ is the reactive species of NBS, a retarding effect of succinimide on the rate of reaction is expected. The increase in the value of k_{obs} with an increase in [succinimide] clearly indicates that NBS itself is the reactive species in the present studies.

On the basis of the above facts and obtained results, the mechanism for the oxidation of hydroxyamine by NBS in alkaline medium is presented in Scheme 1.

Scheme 1

where, R_1, and R_2, represent H and H, respectively, in case of HEA, H and HOCH$_2$CH$_2^-$ respectively, in case of bHEA and HOCH$_2$CH$_2^-$ and HOCH$_2$CH$_2^-$, respectively, in case of tHEA.
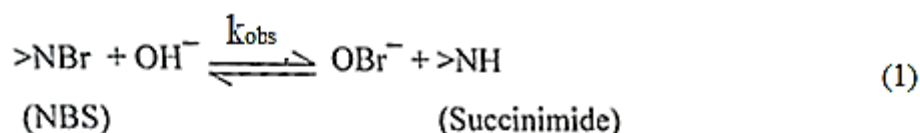
According to Scheme 1, the rate of disappearance of NBS may be given as.

$$-\frac{d[NBS]}{dt} = k[X][OH^-] \qquad \ldots\ldots\ldots\ldots(4)$$

Again,

$$[OBr^-] = \frac{k[NBS][OH^-]}{[succ]} \qquad \text{from step (1)} \qquad \ldots\ldots\ldots (5)$$

$$[X] = K_2[HA][NBS] \qquad \text{from step (2)} \qquad \ldots\ldots\ldots\ldots (6)$$

The total concentration of NBS at any time may be given as:

$$[NBS]_T = [NBS] + [OBr^-] + [x] \qquad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Thus finding the value of [X] in terms of [NBS]$_t$, the rate of disappearance of NBS may be given as

$$-\frac{d[NBS]}{dt} = \frac{kK_1[AA][NBS]_r[Succ.][OH^-]}{[Succ.]\{1 + K_2[AA] + K_1[OH^-]\}} \quad \dots\dots\dots\dots\dots(8)$$

According to rate law (8), the order of reaction in (HA) and $[OH^-]$ should decrease from unity at higher concentrations of hydroxyamine and alkali, respectively. A plot of [succinimide]/k_{obs} versus [succinimide] should be linear with an intercept.

The entropy of activation in each case was found to be negative (reduction of entropy of system) suggesting the compactness of the transition state as compared to the ground state. The nearly same value of $\Delta G^{\#}$ (Table 3) also suggests a common mechanism in case of all the hydroxyamine.

IV.   Conclusion

In view of the experimental results and the kinetic interpretations, it is obvious that the oxidation of hydroxyamines by NBS in alkaline condition leads to the formation of the product. A suitable mechanism is proposed. The effect of oxidant, substrate, alkali shows the reaction rate. A negligible effect of ionic strength of medium was observed. The effect of temperature on the rate of reaction predict the thermodynamic parameters.

References

[1].   Filler R. Oxidation and dehydrogenation with N-bromosuccinimide and related N-haloimides, Chem. Rev. 1963, 63(1), 21–43.
[2].   Mathur N.K., Narang C.K. The Determination of Organic Compounds with N-bromosuccinimide, Academic Press, New York, 1975.
[3].   Sharma J.P., Singh R.N.P., Singh AK. and Singh B., Kinetics and mechanism of Ru(III) catalysed oxidatio In of some polyhydric alcohols by bromosuccinimide in acidic media, Tetrahedron 1986, 42:2739- 2747
[4].   Mavalangi S. K., Nirmala M., Halligudi N, Nandi- bewoor S. T., Ruthenium(III) catalysed oxidation of ethyldiaminetetraacetic acid by N. -bromosucanemide in aquous alkaline medum - A kinetic and mechanistic study,Reaction kinet and catalysis Letter 2001, 72: 391-398.
[5].   Tondon P.K, Singh A.K., Singh J.P., Singh M.P.,. Iridium (III) catalysed oxidation of alcohols in aqueous acidic medium, Oxid· Commun. 2003, 26: 510
[6].   Kalyani P., Teja P.R. Manjari S., Mechanistic investigations of Vanillin Vanilin By N-bromo succinimide - A kinetic Approach, Der Pherma Chemica, 2018, 10(): 128-133.
[7].   Eljack N.D., Mubarakibrahim E, Malik A.A., Alataibi Mohd, Kinetics and mechanism of oxidation of Creatine by N-bromosuccinimide in acidic aquous medium, 2020, 31(3):61-72
[8].   Bhandarkar P.M.R, Mohana K.N., Kinetic and study of mechanistic study of bromination of sulfanilic acid with N-bromosuccinimide in alkaline medium, Bulgarian Chem. Commu. 2010; 42(3): 222-231.
[9].   Khan Parwez AA, Khan A; Asiri A.M., Salman, Studies on the pinative oxidation of levofloxacin. by N-bromosuccinimide in acidic medium and their mechanistic pathway, I of Molecular liquids 2016, 218 604-610
[10].   Feigl F., spot test in organic analysis, London, 1960, p. 130: 214 (1)