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Kinetics and mechanism of oxidation of aminoalcohols with N-Bromopthalimide in aqueous acetic acid

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ABSTRACT

The kinetics of oxidation of amino alcohols (AA), viz., mono ethanolamine (MEA), di ethanolamine (DEA) and tri ethanolamine (TEA) by N-Bromo phthalimide (NBP) in the presence of mercuric acetate have been investigated in aqueous acetic acid medium. The order in [NBP] was found to be unity and fractional order dependence on [substrate] was observed. Michaelis -Menten type mechanism was proposed. Activation parameters have been evaluated.

Keywords: Kinetics, oxidation, amino alcohols, N-Bromopthalimide.

INTRODUCTION

Amino alcohols (AA) are organic bases containing amino and alcoholic functional groups, find extensive applications in the synthesis of surfactants, pharmaceuticals and as addition agents in metal finishing industries [1]. Kinetic results have been reported in literature for the oxidation of amino alcohols by various oxidizing agents[2-6].The N-halo compounds are known to act as sources of halonium ions and these compounds have been used as brominating [7]and oxidizing agents[8, 9]in synthetic organic chemistry as well as analytical reagents especially in acid medium. The N-halo compounds reaction with organic substrates such as anisole, alcohols and amines leads to the products of net oxidation followed by elimination of HBr. Though the oxidation of various organic and inorganic substrates by N-halo compounds has been investigated by several workers [10-13], kinetic study on the oxidation of amino alcohols by NBP is lacking. In view of the above; the present paper reports the studies on the kinetics of the NBP oxidation of ethanolamine, di ethanolamine and triethanolamine in aqueous acetic acid medium.

MATERIALS AND METHODS

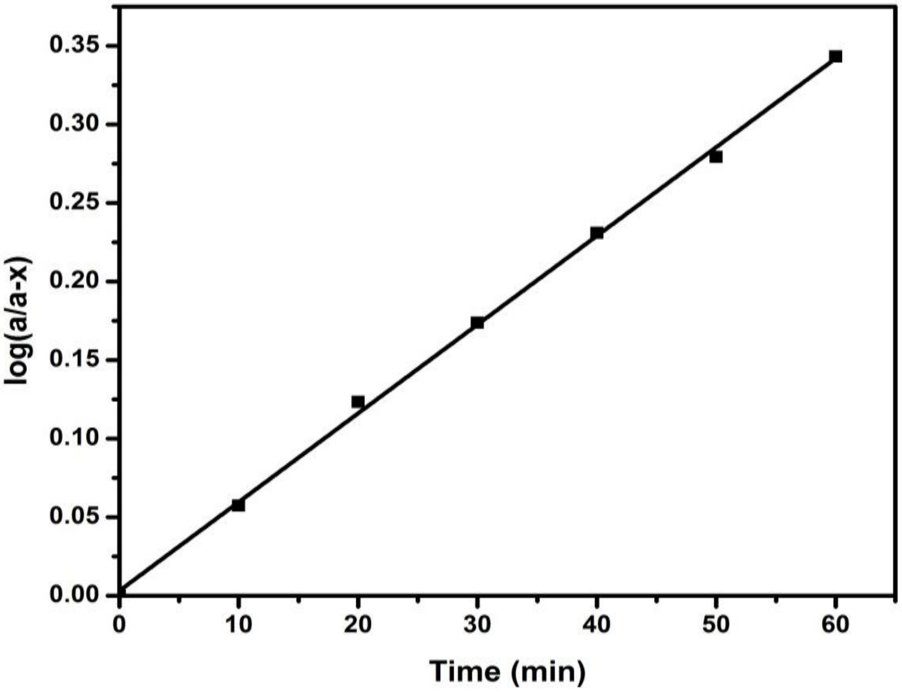
The reagents employed were ethanolamine, di ethanolamine, tri ethanolamine (Merck) and N-Bromopthalimide (Sigma Aldrich). All the chemicals used were of analytical grade. Acetic acid was refluxed with chromic oxide and acetic anhydride for 6 h and then fractionally distilled according to literature procedures [14].The solution of NBP was always prepared freshly and was standardized iodometrically. All aqueous solutions were prepared in doubly distilled water.

Stoichiometry and product analysis: The stoichiometry of the reaction was determined by taking known excess of [NBP] over [amino alcohol] in aqueous acetic acid media at desired temperature. The progress of the reaction was followed for several days to ensure the completion of the reaction. The unreacted [NBS] in aliquots was estimated every day till a constancy in the titer value is obtained. Final analysis indicated that the reactants [NBP]: [MEA], [NBP]: [DEA], [NBP]: [TEA] were found to be 1:1, 2:1, 3:1, respectively. The products of oxidation were identified to be glycolic aldehyde and ammonia from their characteristic spot tests [15] and then by TLC. Ammonia was detected by Nessler's reagent test according to the method of Vogel [16]. Phthalimide (NHP) was the reduced product of NBP.

Kinetic Method: All kinetic measurements were performed under pseudo-first-order conditions with [amino alcohol] at least 10-fold in excess over [NBP] at a constant ionic strength (μ) and desired temperature. The reaction was initiated by mixing previously thermo stated solutions of NBP and amino alcohol, which also contained necessary quantities of acid and mercuric acetate. The progress of the reaction was followed by iodometric determination of the unreacted [NBP] in aliquots of the reaction mixture withdrawn into aqueous KI solutions at regular time intervals. The iodine liberated was titrated against standard hypo solution using starch indicator.

RESULTS AND DISCUSSION

Under the experimental conditions [NBP] <<< [S] (where S denotes the substrate i.e., MEA/DEA/TEA) the linear plot log (a / (a-x)) vs. time, passing through the origin indicated the order in [NBP] to be unity (Figure 1).



[NBP]=1.00×10^{-3}mol dm^{-3}; [MEA] =1.00×10^{-2}mol dm^{-3}; [Hg (OAC) $_2$] = 2.00×10^{-3}mol dm^{-3}; AcOH =30 % (v/v); Temp = 308 K.

Figure 1: Order in [NBP] in the oxidation of MEA by NBP.

It has been reported earlier [17] that Hg (II) can act as a homogeneous catalyst and co-catalyst. The kinetic observations showed that the reaction rate was not affected in the presence of Hg (OAc) $_2$, which negates its role as a catalyst and a co-catalyst in the reaction. The kinetic observations suggest that Hg (OAc)$_2$

acted only as a Br^- scavenger forming $[HgBr_4]^{2-}$ [18]. It has been reported earlier by several workers [19-27] that NBP is good oxidizing and brominating agent due to the presence of the highly polar N-Br bond. The NBP, like other similar N-halo imides, may exist in various forms in acidic medium [28] i.e., free NBP, Br^+, HOBr, and $(H_2OBr)^+$, as per the following equilibria:

$$\text{NBP} + H_2O \rightleftharpoons \text{HOBr} + \text{NHP} \qquad \text{(i)}$$

$$\text{NBP} + H^+ \rightleftharpoons \text{NHP} + Br^+ \qquad \text{(ii)}$$

$$\text{NBP} + H^+ \rightleftharpoons (\text{NBPH})^+ \qquad \text{(iii)}$$

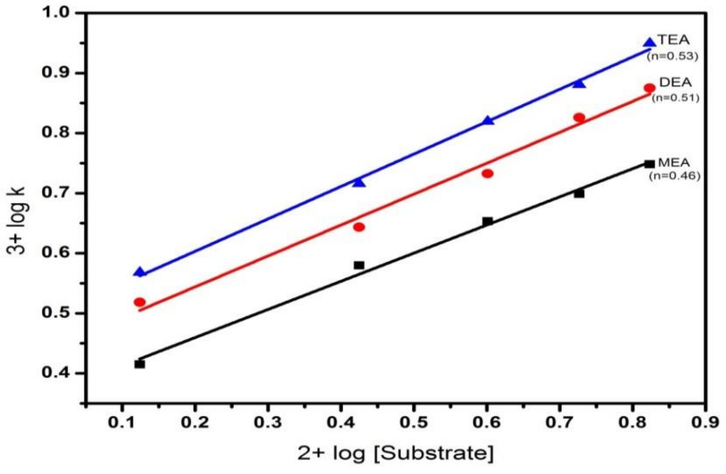
$$\text{HOBr} + H^+ \rightleftharpoons (H_2OBr)^+ \qquad \text{(iv)}$$

In the present investigation, the active species may be N-Bromopthalimide or $(\text{NBPH})^+$. Change in $[NaClO_4]$ showed an insignificant effect. Increase in [phthalimide] showed a marginal increase, increase in $[HClO_4]$ the reaction showed decreasing effect on the rate and varying compositions of solvent showed an insignificant effect (table 1). Hence $(\text{NBPH})^+$ does not participate in the rate-determining step. All these factors indicate that N-Bromopthalimide is the only possible reactive species taking part in the reaction. In the light of experimental results, a suitable mechanism has been proposed.

$$\text{NBP} + [S] \overset{K}{\rightleftharpoons} X \qquad (1)$$

$$X \xrightarrow[k]{H_2O} \text{Products} \qquad (2)$$

Mono ethanol amine (MEA), diethanol amine (DEA), and tri ethanol amine (TEA) were used as substrates in the present study. The plot of log k_{obs} versus log [Substrate] was linear with slope less than unity showing fractional order dependence on [Substrate] (Figure 2). Further, a plot of $1/k_{obs}$ versus 1/ [Substrate] were linear with an intercept on y-axis, confirming the fractional order dependence on [Substrate] (Figure 4).



$[NBP]=1.00\times10^{-3}$mol dm^{-3}; $[Hg(OAC)_2] = 2.00\times10^{-3}$mol dm^{-3}; AcOH =30 % (v/v); Temp = 308 K.

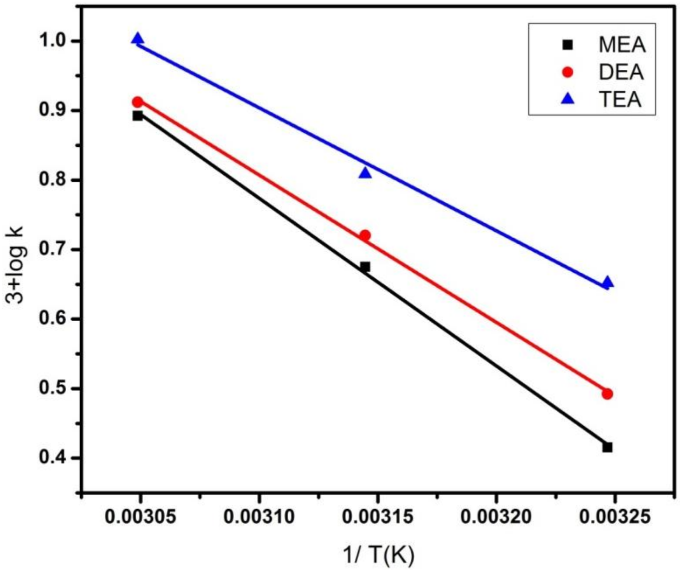
Figure 2: Effect of [Substrate] on k' in NBP-Amino alcohols reactions.

Table 1: Effect of variation of Phthalimide, ionic strength, solvent and $[H^+]$ on the rate of oxidation of MEA by NBP.

[NHP] ×10^2 mol dm^{-3}	**[$NaClO_4$] ×10^2 mol dm^{-3}**	**HOAc % (v/v)**	**[H^+]×10^2 mol dm^{-3}**	**k'×10^3**
0.0	-	-	-	1.2
0.6	-	-	-	1.3
1.3	-	-	-	1.5
2.0	-	-	-	1.7
2.6	-	-	-	1.8
-	**0.6**	-	-	1.2
-	**1.3**	-	-	1.4
-	**2.0**	-	-	1.5
-	**2.6**	-	-	1.6
-	**3.3**	-	-	1.8
-	-	**0.0**	-	1.2
-	-	**13**	-	1.3
-	-	**26**	-	1.4
-	-	**40**	-	1.5
-	-	**53**	-	1.5
-	-	-	**0.0**	1.2
-	-	-	**0.6**	1.0
-	-	-	**1.3**	0.8
-	-	-	**2.0**	0.6
-	-	-	**2.6**	0.5

[NBP]=1.00×10^{-3}mol dm^{-3}; [MEA] = 1.00×10^{-2}mol dm^{-3}; [Hg (OAC) 2] = 2.00×10^{-3}mol dm^{-3};
AcOH =30 % (v/v); Temp = 308 K.

The reaction was studied at different temperatures. It was found that the values of rate constants increasing with increasing temperature and computed activation parameters, namely energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) from Arrhenius plot of log (k) versus (1/T) (Figure3). The data of activation parameters have been compiled in Table 2**.**



[NBP]=1.00×10^{-3}mol dm^{-3}; [MEA] = 1.00×10^{-2}mol dm^{-3}; [Hg (OAC) $_2$] = 2.00×10^{-3}mol dm^{-3}; AcOH =30 % (v/v).

Figure3: Plot of log k versus 1/T for the reactionsof MEA, DEA and TEA.

Table 2: Thermodynamic parameters for the oxidation of MEA, DEA and TEA.

Substrate	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	- $\Delta S^{\#}$ (JK^{-1} mol^{-1})
Monoethanolamine	46.17	43.47	88.61	146.49
Diethanolamine	40.58	37.88	88.16	163.17
Triethanolamine	33.60	31.04	87.22	182.54

[NBP] =1.00×10^{-3}mol dm^{-3}; [MEA] = 1.00×10^{-2}mol dm^{-3}; [Hg (OAc) 2] = 2.00×10^{-3}mol dm^{-3}; AcOH = 30% (v/v).

Mechanism of Oxidation: In order to gain an insight into the mechanistic path, it is essential to know the nature of the reactive oxidizing and reducing species. NBP is known to exist in three forms in acid media, namely, NBP itself, NBPH+ (protonated NBP) and bromonium ion (Br+). Since all the kinetic studies are conducted in the presence of mercuric acetate, the liberated Br_2 during the course of the reaction can be removed in the form of $HgBr_4^{2-}$ or $HgBr_2$ complexes because Hg (OAc) $_2$ acts as a scavenger for Br− formed in the reaction:

$$>NBr+HBr\rightarrow>NH+Br_2....$$

It has been reported earlier **[29]** that the reaction precedes in two stages in the absence of mercuric acetate**.** The first stage of oxidation is due to NBP itself, whereas the second stage is mainly due to oxidation by

Br_2. The pure NBP oxidation can be followed by the initial addition of mercuric acetate which buffer the activity of Br_2 formed in the reaction.

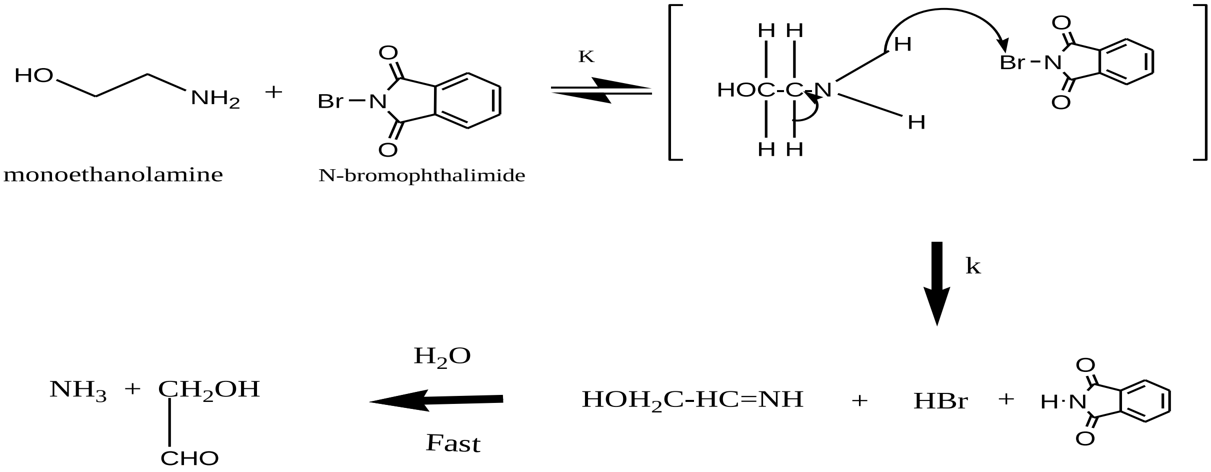
Table 3: Formation constants and rate constants for NBP-amino alcohols reactions at various temperatures.

Substrate	***K***			**10^3 k**		
	308 K	318 K	328 K	308 K	318 K	328 K
MEA	59.281	25.308	13.863	2.602	4.733	7.808
DEA	45.390	21.281	12.912	3.107	5.250	8.160
TEA	27.369	17.140	10.608	4.487	6.438	9.999

[NBP]=1.00×10^{-3}mol dm^{-3}; [Hg (OAC) $_2$] = 2.00×10^{-3}mol dm^{-3}; AcOH =30 % (v/v).

This discussion together with the observed kinetics, the first-order dependence of rate on [NBP] and fractional order on [Substrate] the probable mechanism for the reaction of NBP and MEA (as a typical case) is shown in **Scheme 1.**

Scheme 1



The rate law for the above mechanism can be written as,

$$Rate = \frac{-d[NBP]}{dt} = \frac{kK[S][NBP]}{1+K[S]} \ldots\ldots (1)$$

$$\frac{Rate}{[NBP]} = \frac{kK[S]}{1+K[S]} \ldots\ldots\ldots (2)$$

Since, rate/ [NBP] = k_{obs} (or) k'; equation (2) may be transformed to;

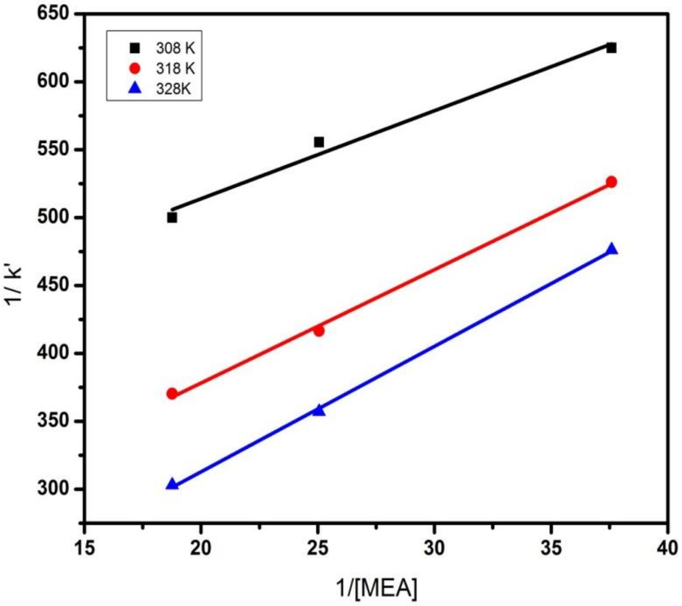
$$k' = \frac{kK[S]}{1+K[S]} \ldots\ldots (3)$$

Taking reciprocals on both sides for equation (3) leads to;

$$\frac{1}{k'} = \frac{1}{kK[S]} + \frac{1}{k} \ldots\ldots (4)$$

(Where, S denotes the substrate)

From equation (4), a plot of 1/k' versus 1/ [EA] should be a straight line with positive intercept on y-axis and which were obtained experimentally (Figure 4), thus supporting the proposed mechanism. Further, the value of k calculated from the corresponding intercept, and also from the ratio of intercept to slope of the line, evaluated the value of K and presented in table 3.



[NBP]=1.00×10^{-3}mol dm^{-3}; [Hg (OAC) $_2$] = 2.00×10^{-3}mol dm^{-3}; AcOH =30 % (v/v).

Figure 4: Effect of [MEA] on k' in NBP-Mono ethanol amine reaction at different temperatures.

APPLICATIONS

Ethanol amines are extensively used in cosmetics, as a plasticizer in polymers, in paints, in the synthesis of surfactants, pharmaceuticals, as addition agents in the metal finishing industry, effective solvents in removing sulfur contaminants from refinery off-gas and in a variety of other applications. Aqueous mono ethanolamine (MEA) is used extensively to remove CO_2 from flue gas and MEA is an important ingredient for food preservative formulations. It is also used to impregnate wood in outdoor applications to guarantee a long life cycle. Di ethanolamine is used as one of the key raw materials in the production of high quality herbicides. Tri ethanolamine is used to produce cement grinding aids and performance enhancer, which reduce energy consumption during the manufacturing process of cement and improve the cement quality.

CONCLUSIONS

The kinetics and mechanism of oxidation of ethanolamine by N-Bromopthalimide in the presence of mercuric acetate has been studied in aqueous acetic acid medium. First order dependence on [NBP] and fractional order dependence on [ethanolamine] was observed. The oxidation products were identified as ammonia and glycolic aldehydes. On the basis of kinetic features, Michaelis - Menten kinetics was adapted to study the effect of [S] on the rate at different temperatures and thermodynamic parameters have been evaluated. The results indicate that the order of reactivity of these compounds is TEA > DEA > MEA. The increased reactivity of TEA over DEA and MEA may be attributed to the increase in the number of hydroxyl-ethyl groups **[30]**, facilitating the hydride ion transfer. It was observed, further, that increasing temperature decreases the value of *K* indicating that the reaction is of an exothermic nature. This is also indicated by the ΔH values for the formation constant *K*.

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