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KINETICS AND MECHANISM OF OXIDATION OF ETHYLENE DIAMINE TETRA ACETIC ACID (EDTA) BY BROMOAMINE-T IN BUFFER MEDIUM

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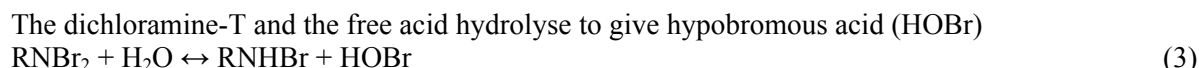E-mail: obeidalsediq@yahoo.com

ABSTRACT

Kinetics and mechanism studies of the oxidation of ethylene di amine tetra acetic acid (EDTA) by bromamine-T (BAT) in acetic buffer of pH 5 have been investigated. The reaction showed first order in [BAT] and fractional order in[EDTA] and [H$^+$]. Addition of reaction product (toluene sulphonamide) or varying the ionic strength of medium has no effect on the rate. A mechanism involving electrophilic attack by positive halogen of BAT at neutral nitrogen of EDTA was proposed.

Keywords: Kinetics**,** Mechanism, Oxidation, bromamine, ethylene diamine tetra acetic acid.

INTRODUCTION

N-bromo toluene sulphonamide (Bromamine-T, BAT) was introduced as analytical reagent for estimation of various reactants in aqueous media[1], and an active oxidant for the oxidation of amino acids[2]. Bromamine-T is analogous to chloramines-T[3-4]and Bromamine-B[5-6] CH3C6H5SO2NHBr(RNHBr) [7], and behaves like a strong electrolyte in aqueous solution. The anion CH3C6H6SO2NBr-, (RNBr-) picks up a proton

RNBr- + H+ ↔ RNHBr   (1)

RNHBr undergo disproportionation
2RNHBr ↔ RNH2 + RNBr2   (2)

The dichloramine-T and the free acid hydrolyse to give hypobromous acid (HOBr)
RNBr$_2$ + H$_2$O ↔ RNHBr + HOBr   (3)
RNHBr + H$_2$O ↔ RNH$_2$ + HOBr   (4)

The reactive species HoBr ionizes as
HOBr ↔ H+ + OBr-   (5)
Ka = 2.0 x 10-9 at 250C

The present article reports our observation on the kinetics of oxidation of ethylene diamine tetra acetic acid by BAT in acetate buffer of pH 5, little is known about the kinetic and mechanism of its oxidation by various oxidants, the oxidant so far tried for the investigation was Ce(IV) [8-9], chloramines-T[10], iron III[11] and sulfuric acid[12].

EXPERIMENTAL

A recrystallised BAT compound[13-14] was used. Solution of BAT was freshly prepared, because decomposition occurs on standing or exposure to light, and for this purpose a brown volumetric flask was used.All UV kinetic measurements were performed using a Py-Unicam PV 8700UV / Vis. Spectrophotometer.

The progress of the reaction was monitored by following the absorbance reading at different time using the standard infinity method. The chosen band used for the kinetic runs was at λmax 265 nm.
BAT was prepared by adding bromine to a solution of p-toluene-sulfonamide in sodium hydroxide[15]. Solution of BAT was prepared daily.

Stoichimetry:
Reaction mixture containing exess of [BAT] over [EDTA] were equilibrated at 250C in the presence of acetate buffer of pH 5. from the estimation of inconsumed BAT, It was observed that one mole of EDTA consumed 8 mol of BAT to give the formic acid. Formic acid was detected by standard methods[16].

RESULTS AND DISCUSSION

At constant [EDTA] and pH, plot of ln [A∞-A_t] versus time are linear indicating a first order dependence of rate on [BAT], (Fig. 1). The rate increases in [EDTA] (table 1) and a plot of log k versus log [EDTA] is linear with slope of 0.41 (Fig. 2). The rate of reaction decreases with increase in pH from 5.0 to 6.2 (table 2). A plot of log k against pH is linear with slope of 0.73 (Fig.3). Addition of the reaction mixture or varying the ionic strength of medium by addition of $NaClO_4$ has no effect on the rate values.
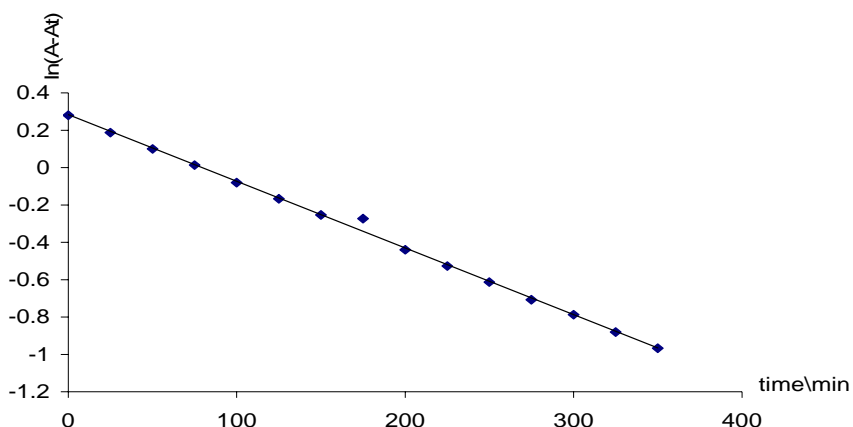
figure(1). plot for determination of the first & order rate constant for BAT oxidation of EDTA at 25c^0. [BAT]=1X10^-4M,[EDTA]=1X10^-3M

Table-1: Kinetic data for the BAT Oxidation of EDTA at 25^0C varying concentration of the reactants at pH = 5.

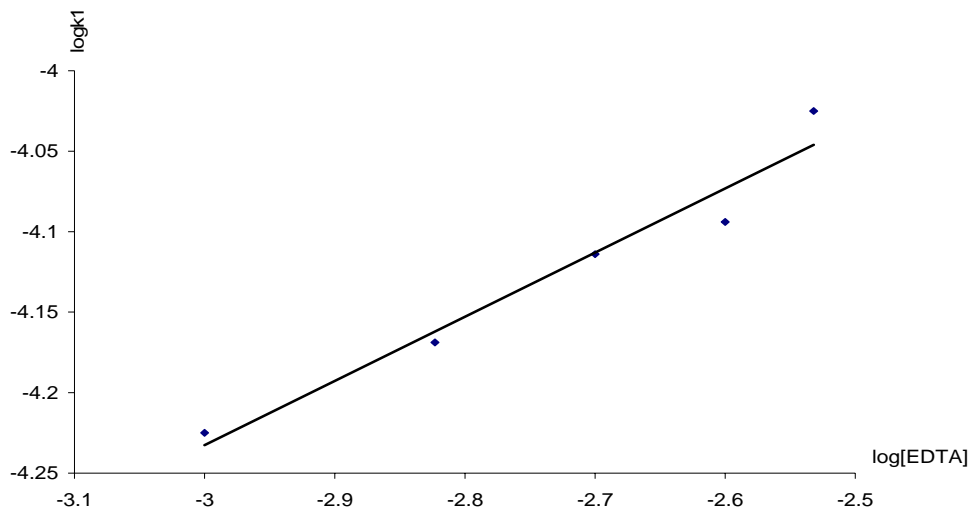| 10^4 (BAT)/M	10^3 (EDTA)/M	$10^5 k/s^{-1}$
1.0	1.0	5.956
1.5	1.0	5.871
2.5	1.0	6.011
1.0	1.5	6.761
1.0	2.0	7.672
1.0	2.5	8.125
1.0	3.0	9.440

Figure 2. plot for determination the order of the reaction in [EDTA] at 25 C and pH =5

Table-2: Kinetic data for the BAT oxidation of EDTA at 25^0C varying pH of solution, [BAT] = $1x10^{-4}$M and [EDTA] = $1x10^{-3}$M

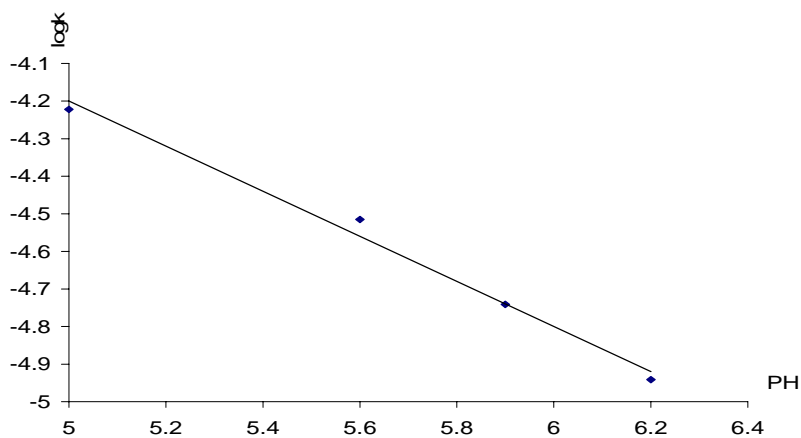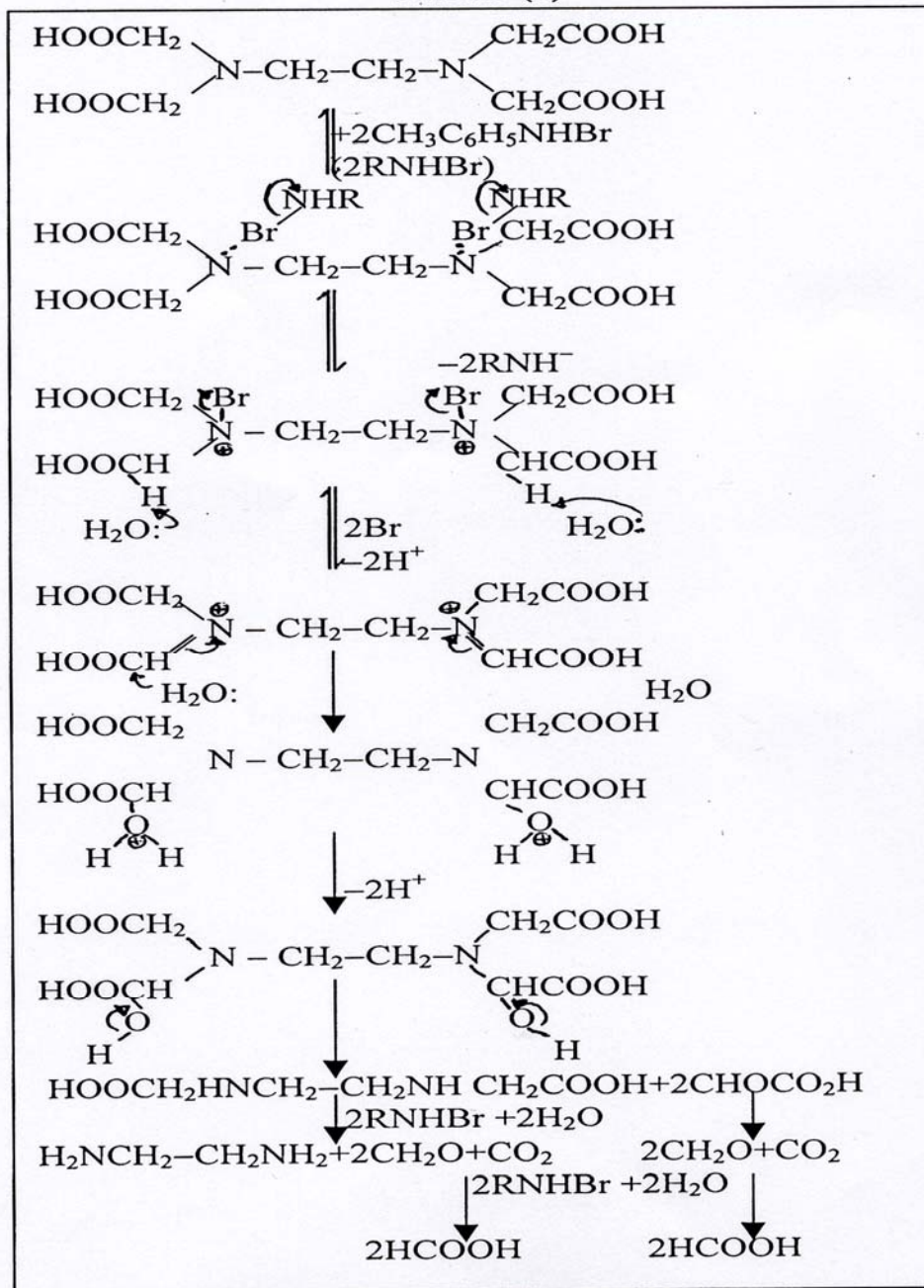| pH	$10^5 k/s^{-1}$
5.0	5.956
5.3	3.715
5.6	3.055
5.9	1.820
6.2	1.135

Figure 3, shows the effect of increasing pH on the rate constant for the reaction of BAT and EDTA at 25 C, BAT conc. = 1x10^-4 and EDTA conc.

scheme (2)

Addition of reaction mixture to acryl amide does not initiate polymerization showing the absence of free radicals. The possible oxidizing species in acidified solution of BAT are RNHBr, RNBr2 and HOBr. If RNBr2 were to be the reactive species, the rate should have been second order with respect to [BAT] which is contrary to experimental observation. If HOBr were to be the reactive oxidant, a first order retardation of the rate by added p-toluene sulfonamide would be expected, but no such effect has been noticed (eq. 4). The dependence of rate on [H+] indicates protonation of oxidant or substrate (eq. 1). Bishop and Jennings (3) have shown in their studies on aqueous solutions of CAT, that at pH 3, the concentration of anion is greater than that of the free acid. Hence a protonation equilibrium (eq. 1) can be

assumed in aqueous BAT solutions in acetate buffer and with neutral EDTA as the substrate. Scheme (1) can be proposed for the oxidation of EDTA with BAT

RNBr- + H+ ↔ RNHBr   (6)
RNHBr + substrate ↔ X   (7)
X → X/   slow and rate determining step.   (8)
X/ + 7 RNHBr → Product   (9)

<div align="center">Scheme-1</div>

According to the above conclusions, the total concentration of BAT equal to [RNBr-], [RNHBr] and [X]. The rate law can be derived

$$\frac{-d[BAT]}{dt} = \frac{K_1K_2K_3\,[BAT][Substrate]\,[H+]}{1 + K_1[H+] + K_1K_2\,[EDTA]\,[H+]} \tag{10}$$

The rate law (10) is in agreement with experimental results, wherein a first order dependence on [BAT] and fractional orders in [Substrate] and [H+] have been observed. Equation (10) can be transformed into the following equation.

$1 / k = (1 / k_3K_2[EDTA]\{(1 / K_1[H+]) + 1\}+ 1 / k_3$ (11)
$1 / k = 1 / [H+]\{1 / k\,K_1K_2[EDTA]\} + \{(1 / k_3K_2[EDTA]) +1 / k_3$ (12)

From the linear double reciprocal plots, $1 / k$ Vs. $1 / [EDTA]$ and $1 / k$ Vs. $1 / [H+]$ values of constants could be calculated and are found to be $10^4 k_3 = 1.219\ s^{-1}$ (eq. 4), $10^{-4}K_1= 13.28\ dm^3\ mol^{-1}$ (eq. 4 and 5 respectively) and $K_2 = 1548\ dm^3\ mol^{-1}$.

The mechanism of oxidation of EDTA by BAT envisages an electrophilic attack by the positive halogen of oxidant at neutral nitrogen which subsequently leads to cleavage of the substrate molecule as shown below.

REFERENCES

1. C. G. R. Nair and P. Iudrasenan., *Talanta* **23**, 239 (1976).
2. N. Y. Salman and K. H. Al- Niami, J. Ibn Al- Haitham , *Pure and applied science*, **1, (II)** 245, (1998).
3. E. Bishop and V. J. Jenings ,*Talanta,* **1**, 197 (1958)
4. D. S. Mahadevapa, S. Ananda, M. B. M. Gowda and K. S. Ranagapa, *J. Indian Chem. Soc.* **LX1**, 323 (1989).
5. N. Y. Salman and K. H. Al- Niami, *J. of college of science* ,**1**, 14 (2001).
6. M. M. Campbell and G. Johnson, *Chem. Rev.,* **78**, 65 (1978).
7. F. E. Handly and J. P. Johnstion, *J. Chem. Soc. Perkin Trans.*, **2,** 742 (1973).
8. S. B. H. Al-Haokimi, W. H. Webb and W. Z. Rcarnoll, *Anal. Chem.*, **246**, 231 (1969).
9. G. H. Rao, *Indian J. Chem,.* **8**,328 (1970).
10. R. Katre, S. K. Solanki Ghanat, K. Joshi and Sangeeta Patil, *Asian J. of Chemistry*, **17(2)**, 1063 (2005).
11. R. J. Motekantis, A. E. Mantell and D. Hayes, *Can. J. Chem.,* **58**, 1999 (1980)
12. M. S. Safarzadeh, D. Moradkhani and M. O. Lkhchi, *J. of Hazzardous Materials*, **163,** 880 (2009).
13. A. J. Vulterine and J. Nagai, *Talanta*, **27**, 25 (1980).
14. A. R. Murthy and B. S. Rao, *Proc. Indian Acad. Sc,* **35**, 69 (1952).
15. F. D. Chattawy, *J. Chem. Soc.*, 145 (1905).
16. F. Felgl, Spot Test in *organic, Analysis, Elsevier, Amsterdam* **40**, 396 (1956).