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RESEARCH ARTICLE

KINETICS AND MECHANISM OF SILVER CATALYSED OXIDATION OF ACETAMIDE BY BAT

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ABSTRACT

The kinetics of Ag+ catalysed oxidation of Acetamide by N-bromoparatoluensulphonamide (BAT) as a oxidant is used. In aquous medium the reaction was carried out. Results from the study shows reaction was found to be of first order with respect to BAT and Acetamide. The specific rate of the reaction increases with an increase in BAT concentration as well as amide concentration, The specific rate is not affected by the addition of allyl acetate, Sodium chloride, PTS and by changing pH. The reaction rate remains constant and at the end the rate of reaction found to be first order. On the basis of these kinetic results, a possible reaction mechanism is proposed and an attempt has also been made to formulate a reaction scheme.

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INTRODUCTION

The Various oxidants used for kinetic study of reactions are chloramines, chloramine-T (CAT) and Chloramine-B (CAB) are reviewed (Campbell and Johnson, 1978) (BAB), (BAT), (CAB), but there is scant information in literature about the bromine analogous. Bromamine-T has been recently used for direct determination of a variety of substances (Gaikwad *et al.*, 2013). We report here in the kinetics of Silver catalysed oxidation of acetamide by bromamine-T (BAT) in alkaline medium. The other oxidants (Adam Hulanicki and Stanisław Głab, 1976) used for the oxidation of amides are potassium permanganate, potassium peroxydisulphate, aqua cations- Ag^{2+}, Co^{3+}, Mn^{3+}. Amides are used (Nrusingha and Khandual, 1991) as antihypertensives, for treatment of heart failure, for inhibition of absorption of dietary cholesterol and in mental disorder treatment. Thus this study has medicinal andbiological importance. This prompted us to undertake this study using silver as catalest.

MATERIALS AND METHODS

Experimental

Bromamine-T solution was prepared by the method of Nair and Indrasenan2 and was standardized iodometrically. Chloramine-T (EMerck) P- toluenesulphonaamide (Koch-light) and cobalt nitrate (EMerk) 3- Nitro Benzamide (E-Merck) were used. All other chemicals were of analytical grade. Double distilled water was used throughout the investigations. The reaction mixture containing substance buffer solution (sodium carbonate and sodium bicarbonate), silver nitrate solution was allowed to equilibriate for half an hour, after which bromamine- T was added to initiate the reaction. The kinetic studies were carried with (amide)>> (BAT) (at least 5-10 times.). A blank experiment was carried out under identical conditions with the substrate (amide) and the result was noticed after 24 hours. The specific rate for self decomposition of BAT was quite negligible. Temperature was recorded after confirmation. The progress of the reactions was monitored for at least two half- lives by examining aliquots of the reaction mixture for unreacted bromamine-T indirectly using ascorbic acid due to interference of liberated iodine in direct titration of BAT. Ascorbic acid is in excess in comparison to BAT in the reaction mixture and it consumes all the amount of BAT. Remaining amount of ascorbic acid was titrated with CAT solution. The volume of unreacted BAT solution in the reaction mixture was obtained by substracting the volume of CAT solution from the blank. Pseudo first order rate constants were obtained All the reactions are carried out in constant temperature water bath with an accuracy of ± 0.005°C with electrical stirrer and heater arrangement.

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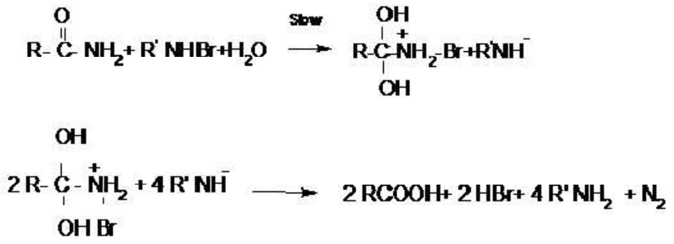
In Stoichiometry and product analysis

Stoichiometry of BAT-amide reaction was determined in presence of buffer solution and Ag^+ ions by equilibrating varying ratio of (BAT) to (amide) at 333K. The stoichiometry of the reaction is 1:1One mole of BAT corresponds to one mole of Amide and the final products are Acetic acid, para toluene sulphonamide (PTS) and nitrogen are the oxidation products. The test for acid was carried according to Feigl (Hurd and Mater De La, 1961; Gaikwad Vikram R Patil, 2014; Feigl Fritz, 1972) PTS was detected by paper chromatography (Hurd and Mater De La, 1961) and nitrogen was tested by lime test (Singh *et al*., 1981; Singh, 1977). Hence the observed stoichiometry may be represented by equation (1)

RESULTS AND DISCUSSION

The kinetic results of the study are shown in Tables-1,2, The values of k calculated by using the relation k calculated= intercept+slope x (Ag+) arein good aggrement with the values of k observed as in Table-2.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 + R'NHBr + H_2O \xrightarrow{Slow} R-\underset{OH}{\overset{OH}{C}}-\overset{+}{N}H_2-Br + R'NH^-$$

$$2R-\underset{OH\,Br}{\overset{OH}{C}}-\overset{+}{N}H_2 + 4R'NH^- \longrightarrow 2RCOOH + 2HBr + 4R'NH_2 + N_2$$

Where R = C6H5

Table 1. Data of kinetic study at [Ag+] x 10 3 M=0.1, Temp. 60°C

[BAT] x 10 2 M =0.1	[Amide] x 10 1 M	k x 10 3 min-1
0.10	0.05	7.82
0.12	0.05	8.28
0.14	0.05	9.51
0.16	0.05	10.18
0.18	0.05	11.37
0.10	0.06	7.36
0.10	0.07	8.84
0.10	0.08	9.28
0.10	0.09	10.47

It may easily be concluded from the Table-1 that the first order specific rate is a function of BAT as well acetamide concentration. It increases with an increase in (BAT) and is governed by the expression log k = -2.4995+308.8 (BAT)o provided that (BAT)o ≠ zero. where as it increases in a linear manner with an increase in (acetamide).

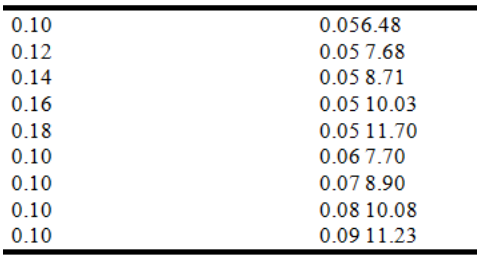
(1)

Where R = C6H5

It may easily be concluded from the Table-1 that the first order specific rate is a function of BAT as well as 3-Nitrobenzamide concentration. It increases with an increase in (BAT) and is governed by the expression log k = -2.4995+308.8 (BAT) o provided that (BAT)o ≠ zero.

Where as it increases in a linear manner with an increase in (3- Nitrobenzamide) and obeys the following relationship.

Table-1: Data of kinetic study at $[Ag^+] \times 10^3$ M=0.1,Temp. 60 ° C
$[BAT] \times 10^2$ M =0.1 [Amide] x 10^1 M K x 10^3 min^{-1}



0.10	0.056.48
0.12	0.05 7.68
0.14	0.05 8.71
0.16	0.05 10.03
0.18	0.05 11.70
0.10	0.06 7.70
0.10	0.07 8.90
0.10	0.08 10.08
0.10	0.09 11.23

Effect of Temperature

The reaction was studied at five different temperatures for the evaluation of various energy parameters and are summarized in Table-3. E. graphically came out to be 13.847 k Cals mole-1ΔH ≠ was calculated by plot of log (KT/h) krvs 1/T on the basis of k= KT x e - ΔH/RT x e ΔS≠/RT/h. The value of E which came out to be 14.174 k cals mole-1 has been used in the following equation to calculate ΔS≠k= KT e ΔS≠/R .e –Ea/RT/h The rate constant for this reaction may be expressed by the following relation. k= 2.117 x 105 x e -14.214/RT sec-1

Table 2. Data of kinetic study at $[Ag^+] \times 10^3$ M=0.1, Temp. 60 ° C

$[BAT] \times 10^2$ M =0.1	[Amide] x 10^1 M	k x 10^3 min^{-1}
0.10	0.05	7.82
0.12	0.05	8.28
0.14	0.05	9.51
0.16	0.05	10.18
0.18	0.05	11.37
0.10	0.06	7.36
0.10	0.07	8.84
0.10	0.08	9.28
0.10	0.09	10.47

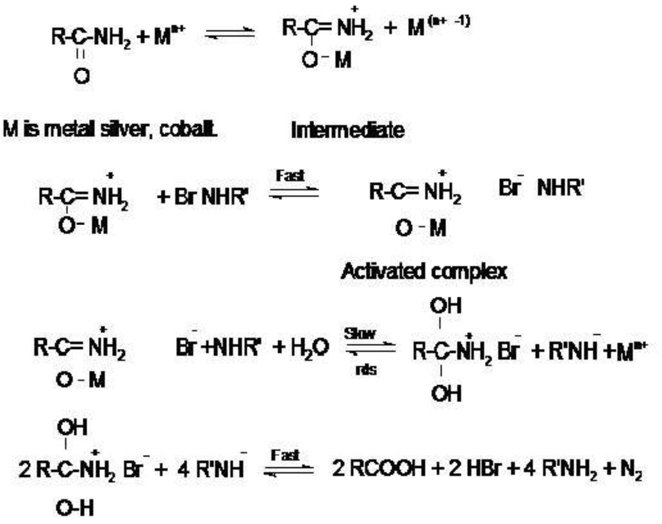
BAT oxidizes methanol, ethanol, dioxan acetone hence effect of solvent composition could not be studied. Low value of frequency factor suggests the effect of addition of salt to the reaction mixture suggesting that rds does not involve any charged species (Gilliom, 1970) and intermediate formation of molecular bromine is ruled out. Zero effect of P.T.S. on the reaction rate indicates that P.T.S is not involved in the post equilibrium step as one of the reaction products and is not probable oxidizing formation of an activated complex (Nimbalkar *et al*., 1990) in the reactions. Fairly high values of ΔG≠ and ΔH≠ indicate highly solvated transition state (Frost and Pearson, 1961; Thimme Gowda and Ishwara Bhat, 19892). There is no species. Similarly RNBr2 (DBT) and HOBr are not real oxidizing species. It also indicates that reaction is not reversible but it might be irreversible one. First order dependence of the reaction on (BAT) suggesting that RNBr2 (DBT) is not the real oxidizing species (Mahadevappa *et al*., 1979).

Table 3. Data of kinetic study at [BAT] x 10^{2} M = 0.1, [Acetamide] x 10^{1} M = 0.05 Temperature 55 ° C 60 ° C 65 ° C

$[Ag^{++}] \times 10^{3}$ M	K x 10^{3} min^{-1}		
Temperature	55 ° C	60 ° C	65 ° C
0.04	2.55	3.12	4.35
0.06	2.72	4.25	5.79
0.08	3.54	5.39	7.21
0.10	4.41	6.53	8.69
0.12	5.71	7.79	10.52
0.14	6.10	8.90	11.76

Mechanism

It was observed that, n o influence of change in pH on the rate of reactionhence H+ ion was observed in rds. The range of pH studied was limited to avoid possibility of hydrolysis of amide which is observed in highly alkaline or acidic medium at high temperature when kept for prolonged time.



Allyl acetate does not affect the rate of a reaction indicating no possibility of free radical mechanism (Mahadevappa *et al*., 1979; Singh Bharat *et al*., 1987). The probable oxidizing species in alkaline solution of BAT (Ephraim Ben-Zvi, 1961) depending up on the pH of the medium RNBr-, RNHBr, HOBr, OBr-. Hypobromite ion (OBr-) may not be involved in the reaction, otherwise reaction would have been immeasurably fast (Duraisamy Thenraja *et al*., 2002). NHBr2 being very unstable, it immediately reacts, with water. So it is not the oxidizing species. It seems more probable that BAT in water gives R'NHBr which further acts real and most predominant oxidising species in this case. If DBT were reactive species, the rate law predicts a second order dependance of the rate on BAT. It is observed that BAT and amide in (1:1) ratio in presence of water react with each other in slow and r.d. step. In presence of catalyst intermediate with amide is formed, due to this decrease in energy of activation. The presence of Ag+ ions in the reaction mixture did not cause any appreciable effect on the rate of parameters. It appears that no reverse reaction or equilibria involving Ag+ is significant (Aparna *et al*., 1998). The formation of Ag++ was proposed by Bawn and Margerisim (Yathirajan *et al*., 1998) and by Srivastava and coworkers by using S2O8 2- oxidant. In our case instead of S2O82- BAT is used as oxidant. BAT forms an activated complex by reacting with an intermediate between amide and Mn+. Taking in to account all the above considerations the following mechanism can be suggested for the cobalt catalyzed oxidation of amide. Conventional reaction scheme may be formulated as under.

Rate = k (activated complex) (H_2O) excess

Overall kinetic order is two, one each in (Amide) and (R'NHBr). The mechanism does not involve any free radical. Thus the mechanism seems to accord with experimental observations and hence acceptable. Thus the reaction mechanism proposed and the derived rate law clearly accounts the experimentaldata.

Conclusion

In the present work, an attempt has been done to study the kinetics of Ag+ catalyzed oxidation of acetamide by sodium salt of Nbromo paratoluensulphonamide (BAT) in aqueous medium. Results from the study indicate that the reaction follows first order with respect to BAT and acetamide. During the study it was also observed that the specific rate of the reaction increases with an increase in BAT concentration as well as amide concentration. However, the specific rate was not affected by the addition of allyl acetate, Sodium chloride, PTS and by changing pH.

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