Original Research Article

Kinetics and mechanism of Silver catalysed oxidation of 3-Nitrobenzamide by BAT

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Abstract

In the present work, the kinetics of Ag^+ catalysed oxidation of 3-Nitro benzamide by sodium salt of N-bromo paratoluensulphonamide (BAT) in aqueous medium has been studied. Results from the study indicate that the reaction was found to be of first order with respect to BAT and 3-Nitro benzamide. It was observed that 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. On the basis of these kinetic results, a possible reaction mechanism is proposed and and an attempt has also been made to formulate a reaction scheme.

1.0 Introduction

The analytical applications and kinetic studies of reactions of the organic chloramines, chloramine-T (CAT) and Chloramine-B (CAB) are reviewed [1] but there is scant information in literature about the bromine analogous. Bromamine-T has been recently used for direct and indirect determination of a variety of substances [2]. We report here in the kinetics of Silver catalysed oxidation of 3-Nitro -Benzamide by bromamine-T (BAT) in alkaline medium . The other oxidants [3] used for the oxidation of amides are potassium permanganate, potassium peroxydisulphate, aqua cations- Ag^{2+}, Co^{3+},Mn^{3+}. Amides are used [4] as antihypertensives, for treatment of heart failure, for inhibition of absorption of dietary cholesterol and in mental disorder treatment. Thus this study has medicinal and biological importance. This promted us to undertake this study.

2.0 Materials and methods
Experimental

Bromamine-T solution was prepared by the method of Nair and Indrasenan[2] and was standardized iodometrically. Chloramine-T (E-Merck) P- toluenesulphonaamide (Koch-light) and cobalt nitrate (E-Merk) 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), cobalt 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 and the values are reproducible within ± 3%.

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.Nitro benzoic acid,para toluene sulphonamide(PTS) and nitrogen are the oxidation products. The test for acid was carried according to Feigl [5-7] PTS was detected by paper chromatography [5] and nitrogen was tested by lime test [8,9].

Hence the observed stoichiometry may be represented by equation (1)

3.0 Results and discussion

The kinetic results of the study are shown in Tables-1,2,3 The values of k calculated by using the relation k calculated= intercept+slope x [Ag^+] are in good aggrement with the values of k observed as in Table-2.
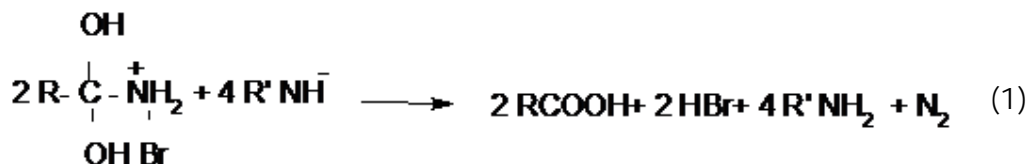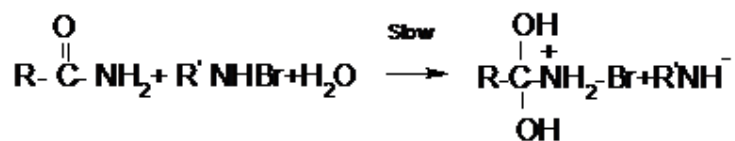
Where R = C_6H_5

Table-1: Data of kinetic study at [Ag$^+$] x 10^3 M=0.1,Temp. 60 ^{o} C

[BAT] x 10^2 M = 0.1	[$C_6H_5CONH_2NO_2$] x 10^1 M	k x 10^3 min^{-1}
0.10	0.05	6.48
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

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.

$$k= \frac{0.1286[\ C_6H_5CONH_2NO_2]_o}{0.0941+ [\ C_6H_5CONH_2NO_2]_o}$$

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^{-1}ΔH$^{\neq}$ was calculated by plot of

log (KT/h) kr vs 1/T on the basis of $k= \frac{KT}{h} \times e^{-\Delta H^{\neq}/RT} \times e^{\Delta S^{\neq}/R}$

The value of E which came out to be 14.174 k cals mole^{-1} has been used in the following equation to calculate $\Delta S^{\neq}$

$$k= \frac{KT}{h} \, e^{\Delta S^{\neq}/R} \, . e^{-Ea/RT}$$

The rate constant for this reaction may be expressed by the following relation.

k= 2.117 x 10^5 x e$^{-14.214/RT}$ sec^{-1}

Table-2: Data of kinetic study at [BAT] x 10^2 M = 0.1   , [3-Nitrobenzamide] x 10^1 M = 0.05

Temperature	55 ^{o} C	60 ^{o} C	65 ^{o} C
[Co^{++}] x 10^3 M	K x 10^3 min^{-1}		
0.04	2.10	3.10	4.25
0.06	2.90	4.26	5.70
0.08	3.68	5.35	7.20
0.10	4.47	6.48	8.61
0.12	5.25	7.69	10.10
0.14	6.05	8.83	11.55
Intercept	0.50 x 10^{-3}	0.8 x 10^{-3}	1.30 x 10^{-3}
Slope	4.090	5.917	7.727

Table-3: Data of kinetic study at [BAT] x 10^2 M = 0.1, [Ag$^+$] x 10^3 M=0.1, [3-Nitrobenzamide] x 10^1 M = 0.05

Temp in ^{0}A	k x 10^3 min^{-1}	Temp. coefficient	Energy of activation ΔE	Frequency factor Ax 10^5	Entropy of activation ΔS	Free energy ΔG	Enthalpy ΔH
328	4.47	-	-	2.077	-28.244	22.787	
333	6.48	1.926	14.443	2.170	-28.186	22.898	
338	8.68	1.773	13.001	2.100	-28.281	23.061	13.619
343	11.49	1.905	15.077	2.060	-28.300	23.216	
348	16.41	-	-	2.180	-28.260	23.255	
Mean	-	1.868	14.147	2.117	-28.266	23.047	

ΔE in kcals mole^{-1}, Frequency factor Ax 10^5 in lit mole^{-1} sec^{-1}, Free energy $\Delta G^{\neq}$ in kcals mole^{-1}, Entropy of activation $\Delta S^{\neq}$ in E.U, Enthalpy $\Delta H^{\neq}$ in kcals mole^{-1}
**graphically**

BAT oxidizes methanol, ethanol, dioxan acetone hence effect of solvent composition could not be studied. Low value of frequency factor suggests the formation of an activated complex [10] in the reactions. Fairly high values of $\Delta G^{\neq}$ and $\Delta H^{\neq}$ indicate highly solvated transition state [11,12]. There is no

effect of addition of salt to the reaction mixture suggesting that rds does not involve any charged species [13] 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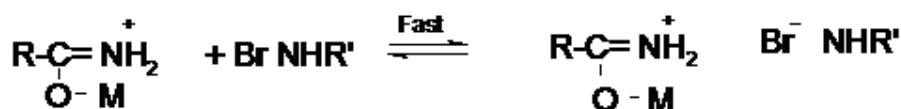 of the reaction products and is not probable oxidizing species. Similarly RNBr$_2$ (DBT) and HOBr are not real oxidizing species. It also indicates that reaction is not reversible but it might be irreversible one. First order dependence of the reaction on [BAT] suggesting that RNBr$_2$ (DBT) is not the real oxidizing species [14].
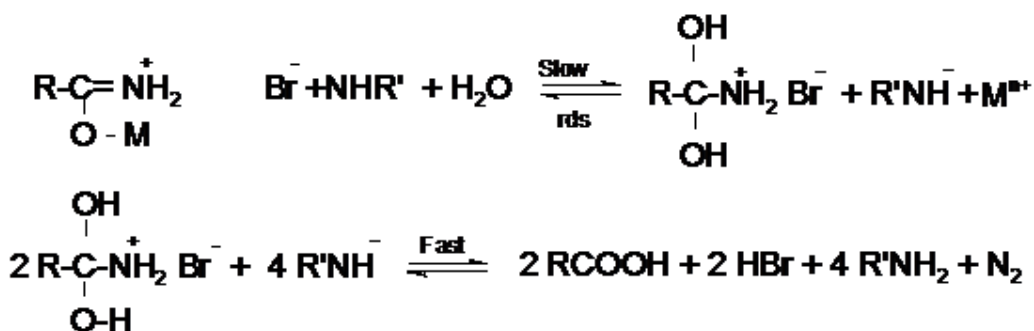
Mechanism

$$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2 + M^{a+} \rightleftharpoons R\text{-}\underset{\underset{O^-M}{|}}{C}=\overset{+}{N}H_2 + M^{(a+\ -1)}$$
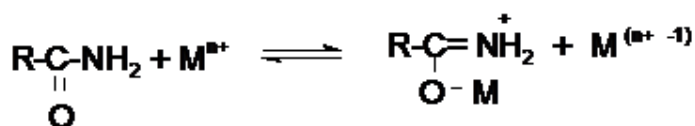
M is metal silver, cobalt.   **Intermediate**

$$R\text{-}\underset{\underset{O^-M}{|}}{C}=\overset{+}{N}H_2 + \overset{-}{Br}\,NHR' \overset{Fast}{\rightleftharpoons} R\text{-}\underset{\underset{O^-M}{|}}{C}=\overset{+}{N}H_2 \quad \overset{-}{Br}\,NHR'$$

Activated complex

$$R\text{-}\underset{\underset{O^-M}{|}}{C}=\overset{+}{N}H_2 \quad \overset{-}{Br}+NHR' + H_2O \overset{Slow}{\underset{rds}{\rightleftharpoons}} R\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}\overset{+}{N}H_2\,\overset{-}{Br} + R'N\overset{-}{H} + M^{a+}$$

$$2\,R\text{-}\underset{\underset{O\text{-}H}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}\overset{+}{N}H_2\,\overset{-}{Br} + 4\,R'N\overset{-}{H} \overset{Fast}{\rightleftharpoons} 2\,RCOOH + 2\,HBr + 4\,R'NH_2 + N_2$$

It was observed that,n o influence of change in pH on the rate of reaction- hence 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 [14,15]. The probable oxidizi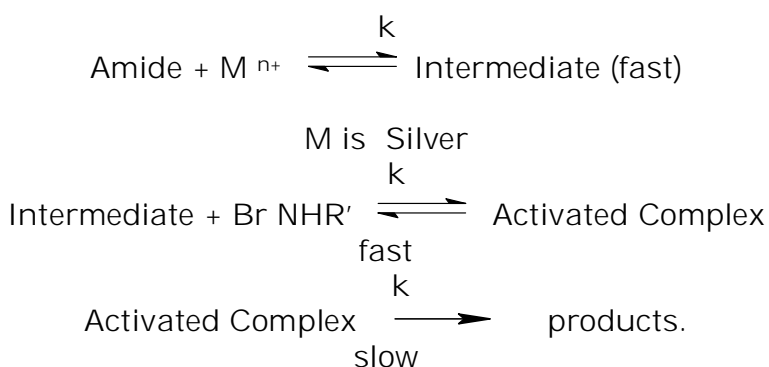ng species in alkaline solution of BAT [16] depending up on the pH of the medium RNBr$^-$, RNHBr, HOBr, OBr$^-$. Hypobromite ion (OBr$^-$) may not be involved in the reaction, otherwise reaction would have been immeasurably fast [17] .NHBr$_2$ being very unstable, it immediately reacts, with water. So 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 [18]. The formation of Ag^{++} was proposed by Bawn and Margerisim [19] and by Srivastava and coworkers by using $S_2O_8^{2-}$ oxidant. In our case instead of $S_2O_8^{2-}$ 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

$$\text{Amide} + M^{n+} \underset{}{\overset{k}{\rightleftharpoons}} \text{Intermediate (fast)}$$

M is Silver

$$\text{Intermediate} + Br\,NHR' \underset{\text{fast}}{\overset{k}{\rightleftharpoons}} \text{Activated Complex}$$

$$\text{Activated Complex} \underset{\text{slow}}{\overset{k}{\longrightarrow}} \text{products.}$$

The following rate equation may be derived for the above mechanism in terms of consumption of BAT.

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 experimental data.

4.0 Conclusion

In the present work, an attempt has been done to study the kinetics of Ag^+ catalyzed oxidation of 3-Nitro benzamide by sodium salt of N-bromo paratoluensulphonamide (BAT) in aqueous medium. Results from the study indicate that the reaction follows first order with respect to BAT and 3-Nitro benzamide. 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.

Acknowledgement

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