

Research Article

Kinetics and Mechanism of Cobalt Catalysed oxidation Reactions in Aqueous Alkaline Medium (Oxidation of Amides by Bromamine-T)

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ABSTRACT

Kinetics and mechanism of oxidation of amides by bromamine-T has been investigated in aqueous medium. Uncatalysed reaction is not possible. We have used Co^{++} as a catalyst. The rate followed first order kinetics in [BAT] and [Amide]. Externally added reaction products and NaCl had no effect on the reaction. Effects by the addition of allyl acetate and change in pH of the reaction medium on the rate have been also investigated. The rate constants for the rate controlling step have been calculated as functions of temperature. The activation parameters have been computed using these constants. The mechanism in which bromamine-T reacts with an intermediate formed by the amide with catalyst in the slow and rate determining step has been proposed.

Keywords: Oxidation, BAT, Amides, Cobalt catalyst, Kinetics and mechanism.

INTRODUCTION

Bromamine-T has been recently used for direct and indirect determination of a variety of substances¹. But it is less used in the field of amide chemistry which plays very important role in medicinal and industrial fields² now a days. In continuation of our previous work^{3,4} we report here the kinetic investigation of oxidation of some substituted amides by bromamine-T (BAT).

EXPERIMENTAL

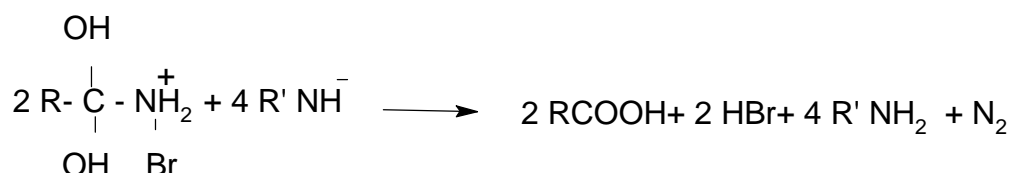
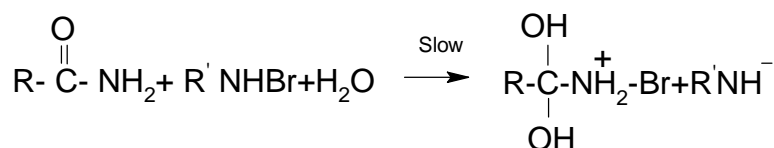
Both the amides were of E-merk quality and their purity was checked by their boiling points. Bromamine-T solution was prepared by the method of Nair and Indrasenan¹ and was standardised iodometrically and stored in amber coloured bottles. Other chemicals were of analytical grade. Double distilled water was used. The experiment was carried out in glass stoppered Pyrex flask whose outer surface was coated with black to eliminate photochemical effect.

The reaction mixture containing amide, Buffer solution, catalyst was allowed to equilibrate for half an hour, after which the bromamine-T solution was added to initiate the reaction. The kinetic study was carried with [Amide] \gg [BAT] (at least 5-10 times). A blank experiment was carried out under identical conditions without the substrate and the result was noticed after 24 hours. The specific rate of self decomposition of BAT was quite negligible. The process of the reaction was monitored at least two half lives by examining aliquots of the reaction mixture for unreacted bromamine-T, indirectly used ascorbic acid, due to interference of liberated iodine in direct titration of BAT. Ascorbic acid which is in excess of BAT, 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 subtracting the volume of CAT solution from the blank. Pseudo first order rate constants were computed (reproducible within $\pm 3\%$).

Stoichiometry and product analysis

The stoichiometry of BAT- amide reaction was determined in presence of buffer solution and the catalyst by allowing the reaction of BAT and amide in different ratios to go to completion. Determination of unreacted BAT in the reaction mixture shows that every mole of amide oxidized; one mole of BAT was consumed.

The observed stoichiometry may be represented as:



(1)

Where R represents N- Ethyl and N,N-Dimethyl in N- Ethyl Acetamide and N,N- Dimethyl Acetamide respectively.

R' represents P- CH₃.C₆H₄.SO₂

In end product analysis, the detection of P- toluene sulphonamide was done by pc and acids by Feigl⁵ and long A.G.⁶. Nitrogen was tested by lime test^{7,4}

RESULTS AND DISCUSSION

The kinetic results of the study are shown in Tables 1,2,3. Plots of [catalyst] versus k show linear straight lines passing through origin, suggesting that uncatalysed reaction is not possible⁸. The values of slopes and intercepts for these plots are shown in Table-3.

The values of k calculated by using the relation k calculated = intercept + slope x [catalyst] are in good agreement with the values of k observed as in TABLE - 1

It may easily be concluded from TABLE -1 that the first order specific rate is a function of BAT as well as amide concentration. It is governed by expression.

$$\begin{array}{ll} \log k = -2.4575 + 30.55 [\text{BAT}]_0 & \text{for N-Ethyl Acetamide} \\ \log k = -2.4350 + 27.77 [\text{BAT}]_0 & \text{for N,N- Dimethyl Acetamide} \end{array}$$

provided that [BAT] ≠ 0

Whereas k increases in a linear manner with an increase in [Amide] and obeys the following relationship.

$$k = \frac{0.056[\text{Amide}]_0}{0.734 + [\text{Amide}]_0} \quad \text{for N-Ethyl Acetamide}$$

$$k = \frac{0.200[\text{Amide}]_0}{2.674 + [\text{Amide}]_0} \quad \text{for N,N Dimethyl Acetamide.}$$

Plots of log (-dc/dt) vs log [Amide] and log (-dc/dt) vs log[BAT] were linear with unit slope indicating first order dependence of rate on the amide as well as BAT concentration.

This order is also confirmed by Van't Hoff equation i.e.

$$\text{order } n = \frac{\log [-dc_1/dt] - \log [-dc_2/dt]}{\log c_1 - \log c_2}$$

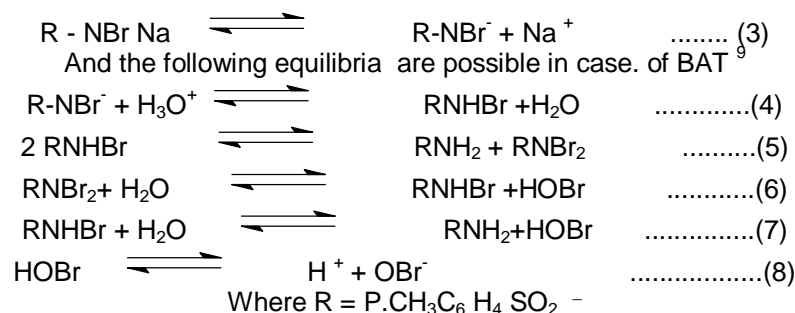
The rates were measured at different temperatures and activation parameters were computed. (TABLE -1).

Addition of NaCl as well as Allyl Acetate had no effect on the rate. The pH of the reaction mixture was varied from 8.88 to 10.60 and the reaction rate was found unaffected (TABLE-2)

Addition of reaction products P- toluene sulphonamide had no influence on the rate.

BAT oxidizes methanol, ethanol, dioxan, acetone, hence effect of solvent composition could not be studied.

Bromamine-T behaves like a strong electrolyte in aqueous solutions dissociating as



The probable oxidizing species in alkaline solution of BAT¹⁰ depending upon the pH of the medium are RNBr⁻, RNHBr, HOBr, OBr⁻.

Addition of sodium chloride had no effect on the rate of oxidation, suggesting that the rate determining step does not involve any charged species¹¹ and intermediate formation of molecular bromine is ruled out.

No effect of addition of paratoluenesulphonamide on reaction rate in indicating that RNBr₂ (DBT) and HOBr are not real oxidizing species. and the reaction might be irreversible one.

No effect of allyl acetate on the rate of reaction indicating no possibility of free radical mechanism^{12,13}.

If HOBr is involved as oxidizing species a first order retardation of the rate by the added PTS is expected.¹⁴

Hypobromite ion (OBr⁻) may not be involved in the reaction, otherwise reaction would have been immeasurably fast.¹⁵

No influence of change in pH on the rate of reaction-hence H⁺ ion is not involved in rds.

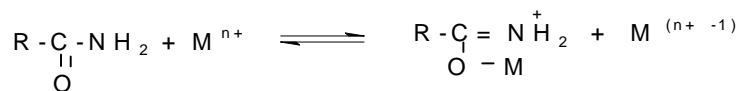
NH₂Br being very unstable, it immediately reacts with water. So it is not the oxidizing species. It seems more probable that BAT in water gives R'NHBr which further acts real and most predominant oxidizing species.

Low value of frequency factor suggests the formation of activated complex¹⁶ in the reactions. Fairly high values of ΔG[‡] and ΔH[‡] indicate highly solvated transition state^{17,18}. While the large negative value of entropy of activation, (ΔS[‡]) suggests the formation of a rigid transition state.

The formation of Ag⁺⁺ ions was proposed by Bawn and Margersim¹⁹ and by Srivastava and coworkers. The presence of Co⁺⁺ ions in reaction mixture did not cause an appreciable effect on the rate of parameters. It appears that no reverse reaction or equilibria involving Co⁺⁺ is significant²⁰.

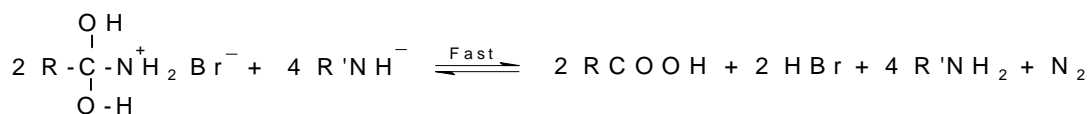
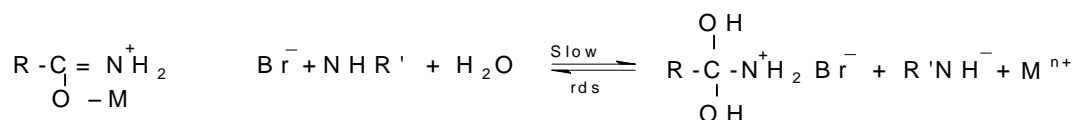
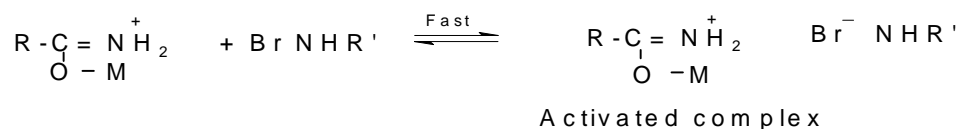
BAT forms an activated complex by reacting with an intermediate between amide and metal ions.

Taking in to account all the above considerations the following mechanism can be suggested for the silver catalyzed oxidation of amides.

Mechanism

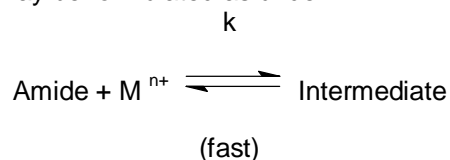
M is metal silver

Intermediate

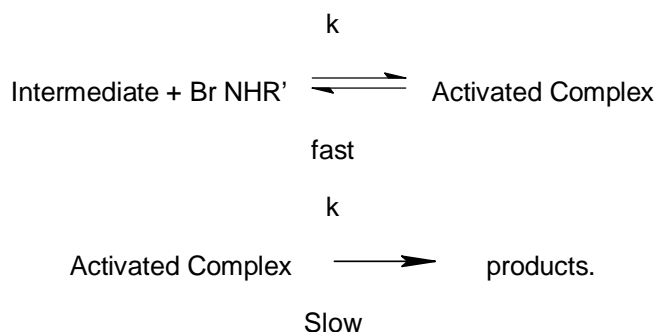


The specific rate of N, N –Dimethyl acetamide is smaller than that of N-Ethyl acetamide. It is because of methyl groups decrease positive charge on carbonyl carbon hence methyl groups are electron donating.

Conventional reaction scheme may be formulated as under:



M is Metal Silver.



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

Rate = k (activated complex) (H₂O) excess

Overall kinetic order is two, one in each (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.

Table 1: Effect of Variation of [Oxidant] [Amide] [Catalyst] and Temperature on Reaction Rate

Temp. = 60°C and pH 8.88 (Unless otherwise Specified)

CATALYST = [Co⁺⁺] x 10² M = 1.0

[BAT] x 10 ² M	[AMIDE] * x 10 ¹ M	k ₁ x 10 ³ min ⁻¹	k ₂ ** x 10 ³ min ⁻¹
	N- Ethyl / N,N- Dimethyl	N- Ethyl	N,N- Dimethyl
1.0	1.0	6.83	7.24
1.2	1.0	7.97	8.59
1.4	1.0	7.73	9.80
1.6	1.0	8.95	11.25
1.8	1.0	10.37	12.65
1.0	1.2	11.86	8.63
1.0	1.4	9.18	10.01
1.0	1.6	10.25	11.36
1.0	1.8	11.30	12.70
1.0	1.0	8.12 ^p	4.32 ^p
1.0	1.0	9.46 ^q	5.76 ^q
1.0	1.0	10.84 ^r	8.64 ^r
1.0	1.0	12.12 ^s	10.13 ^s
1.0	1.0	5.18 ^a	4.95 ^a
1.0	1.0	10.27 ^b	9.75 ^b
1.0	1.0	13.95 ^c	14.34 ^c
1.0	1.0	19.90 ^d	19.31 ^d

*N- Ethyl = N- Ethyl Acetamide

N,N – Dimethyl Acetamide

** [Co⁺⁺] x 10² M = P 1.2, ^a 1.4, ^r 1.6, ^s 1.8

Temp = ^a 55 °C, ^b 60 °C ^c 65 °C ^d 75 °C

	N- Ethyl	N,N – Dimethyl
Ea (kJ mol ⁻¹)	78.95	68.15
A(s ⁻¹)	3.58 x 10 ⁶	7.35 x 10 ⁵
ΔS [‡] (Jk ⁻¹ mol ⁻¹)	-91.80	-110.38
ΔH [‡] (kJ mol ⁻¹)	64.53	72.48
ΔG [‡] (kJ mol ⁻¹)	96.27	98.45

Table 2: effect of salt, pH, and Allyl Acetate on reaction rate

Temp. = 60°C and pH 8.88 (unless otherwise specified)

[BAT] x 10² M = 1.0, [Amide] x 10¹ M = 1.0, [Co⁺⁺] x 10³

M = 1.0 for I [Co⁺⁺] x 10² M = 1.0 for II

[NaCl] x 10 ² M	k ₁ x 10 ³ min ⁻¹	k ₂ ** x 10 ³ min ⁻¹
	I= N- Ethyl Acetamide	II= N,N- Dimethyl Acetamide
NIL	6.83	7.24
1.0	7.02	8.04
4.0	6.55	7.69
7.0	6.36	6.65
10.0	6.21	6.60
Nil	6.96 ^l	7.36 ^l
Nil	6.41 ^k	7.56 ^k
Nil	6.22 ^j	7.56 ^j
Nil	6.34 ^m	6.91 ^m
Nil	6.42 ^w	6.74 ^w
Nil	6.60 ^x	7.37 ^x
Nil	6.25 ^y	6.94 ^y
Nil	6.97 ^z	6.72 ^z

** pH = ^j 9.57, ^k 9.84, ^l 10.20, ^m 10.60

[Allyl Acetate] x 10² M = ^w 1.0, ^x 1.4, ^y 1.8, ^z 2.0

Table 3:

Temperature °C	Intercept		Slope	
	Amide		Amide	
	N- Ethyl	N,N- Dimethyl	N- Ethyl	N,N- Dimethyl
55	0	0	0.529	0.500
60	0	0	0.697	0.700
65	0	0	1.000	1.000

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