Chemical Science Kinetics of Cobalt Catalysed Oxidation of Acetamide by BAT

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Abstract: The kinetics of Co^{++} catalysed oxidation of Acetamide by sodium salt of N-bromo paratoluensulphonamide (BAT) in aqueous medium has been studied. The reaction is found to be first order each w.r.t. BAT and Acetamide. The specific rate increases with an increase in BAT concentration as well as in amide concentration. The specific rate is linearly related to $[Co^{++}]$. by an expression $k = 1.0 \times 10^{-3} + 6.50 [Co^{++}]$.

The specific rate is not affected by the addition of allyl acetate, Sodium chloride, P.T.S. and by changing pH'. The energy of activation, frequency factor, and free energy and entropy of activation respectively are 15.071 kcals $mole^{-1}$, 9.24×10^{-5} lit $mole^{-1}sec^{-1}$, 22.95 kcals $mole^{-1}$ and -25.34 E.U. The mole ratio is found to be 1 mole of BAT to 1 mole of Acetamide. The final products are Acetic acid, paratoluenesulphonamide and nitrogen. 'On the basis of these kinetic results a possible reaction mechanism has been proposed and conventional reaction scheme is formulated.

Key Words: Oxidation, BAT, Kinetics and mechanism, Amides, Cobalt catalyst.

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 cobalt catalysed oxidation of Acetamide 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.

Experimental

Bromamine-T solution was prepared by the method of Nair and Indrasenan[2] and was standardised 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 Co^{++} ions by equilibrating varying ratio of [BAT] to [amide] at 333K.

Acetic acid,paratoluenesulphonamide(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]
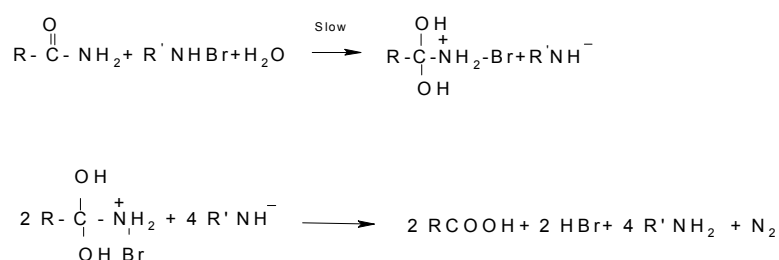
Hence the observed stoichiometry may be represented by equation (1)

(1)
Where R = C_6H_5

Results

The kinetic results of the study are shown in Tables 1,2,3 It seems from the plot of $[Co^{++}] \times 10^3$ M versus $k \times 10^3$ min^{-1} Fig-3 that, linear straight lines are not passing through origin. It suggests that uncatalysed reaction is possible.[10] The values of slopes and intercepts for the lines from Fig-3 are shown in TABLE-2.

The values of k calculated by using the relation

k calculated= intercept+slope x $[Co^{++}]$ are in good aggrement with the values of k observed as in TABLE-2.

It may easily be concluded from the TABLE-1 that the first order specific rate is a function of BAT as well as Acetamide concentration. It increases with an increase in [BAT] and is governed by the expression log k = -2.45+32.50$[BAT]_o$ provided that $[BAT]_o \neq$ zero.

where as it increases in a linear manner with an increase in [3- Nitrobenzamide] and obeys the following relationship.

$$k= \frac{0.0599[CH_3CONH_2]_o}{0.72+ [CH_3CONH_2]_o}$$

Effect of Temperature: The reaction was studied at five different temperatures for the evaluation of various energy parameters and are summarized in TABLE-3.

Table -1

[Co^{++}] x 10^3 M=0.1 Temp. 60 ^{o} C

[BAT] x 10^2 M = 0.1	[C$_6$H$_5$CONH$_2$NO$_2$] x 10^1 M	k x 10^3 min^{-1}
0.10	0.1	7.32
0.12	0.1	8.65
0.14	0.1	9.95
0.16	0.1	11.07
0.18	0.1	12.69

Table -2

[BAT] x 10^2 M = 0.1 [Acetamide] x 10^1 M = 1.0

Temperature	55 ^{o} C	60 ^{o} C	65 ^{o} C
[Co^{++}] x 10^3 M	K x 10^3 min^{-1}		
0.4	2.32	3.75	4.75
0.6	3.19	4.78	6.42
0.8	4.02	6.02	8.18
0.10	4.89	7.32	9.78
0.12	5.78	8.70	11.37
Intercept	0.6 x 10^{-3}	1.0 x 10^{-3}	1.4 x 10^{-3}
Slope	4.58	6.50	8.57

Table -3

[BAT] x 10^2 M = 0.1, [Co^{++}] x 10^3 M=0.1, [Acetamide] x 10^1 M = 1.0

Temp in ^{0}A	k x 10^3 min^{-1}	Temp. coefficient	Energy of activation ΔE in kcals mole^{-1}	Frequency factor Ax 10^5 in lit mole^{-1} sec^{-1}	Entropy of activation $\Delta S^{\neq}$ in E.U.	Free energy $\Delta G^{\neq}$ in kcals mole^{-1}	Enthalpy $\Delta H^{\neq}$ in kcals mole^{-1} graphically
328	4.89	-	-	9.10	-25.34	22.73	
333	7.32	2.00	15.270	9.50	-25.24	22.82	
338	9.78	1.84	13.860	9.10	-25.375	22.98	16.016
343	13.48	1.99	16.083	9.02	-25.42	23.10	
348	19.46	-	-	9.47	-25.33	23.14	
Mean	-	1.94	15.071	9.24	-25.34	22.96	

E. graphically came out to be 16.016 k Cals mole^{-1} $\Delta H^{\neq}$ was calculated by plot of   log $\left(\dfrac{k}{KT/h} \right)$

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

The value of E which came out to be 15.071 k cals mole^{-1} has been used in the following equation to calculate $\Delta S^{\neq}$

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

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

k= $9.24 \times 10^5 \times e^{-15.071/RT}$ sec^{-1}

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

Discussion :

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 RNBr2 (DBT) is not the real oxidizing species.[14]

No influence of change in pH on the rate of reaction- hence H$^+$ ion is not involved 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.
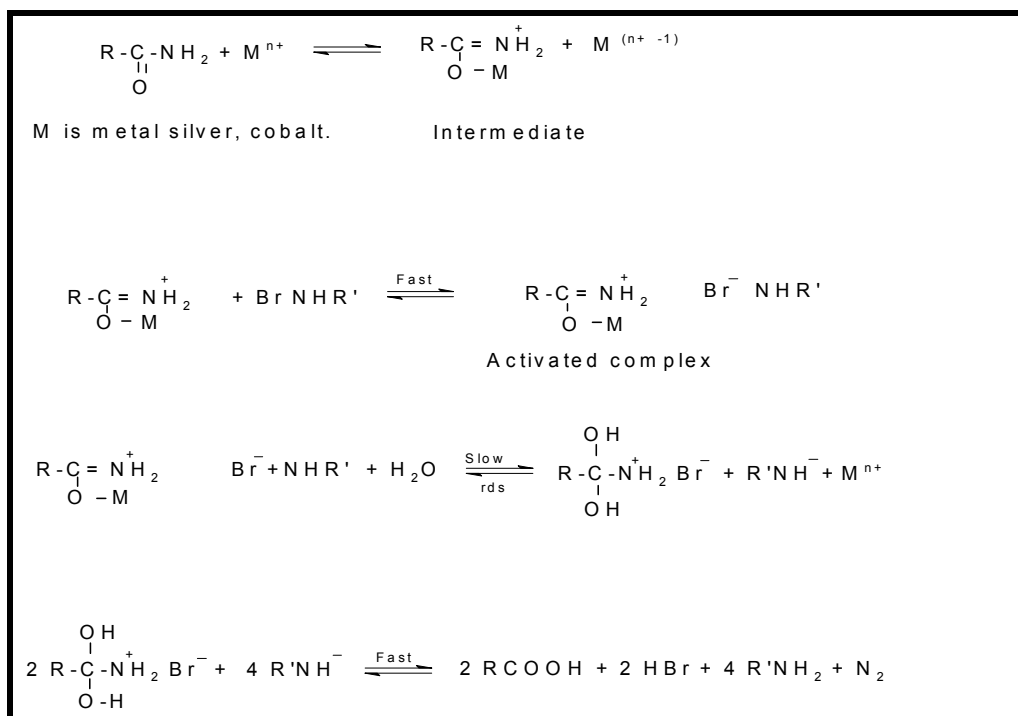
Allyl acetate does not affect the rate of a reaction indicating no possibility of free radical mechanism.[14],[15,] The probable oxidizing species in alkaline solution of BAT[16] depending up on the pH of the medium RNBr$^-$, RNHBr, HOBr, OBr$^-$.

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.
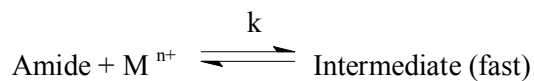
In presence of catalyst intermediate with amide is formed, due to this decrease in energy of activation. The presence of Co^{++} ions in the reaction mixture did not cause any appreciable effect on the rate of parameters. It appears that no reverse reaction or equilibria involving Co^{++} is significant.[18] The formation of Ag^{++} was proposed by Bawn and Margerisim[19] and by Srivastava and coworkers by using S$_2$O$_8$ $^{2-}$ oxidant. In our case instead of S$_2$O$_8$$^{2-}$ BAT is used as oxidant.

BAT forms an activated complex by reacting with an intermediate between amide and M^{n+} Taking in to account all the above considerations the following mechanism can be suggested for the cobalt catalyzed oxidation of amide.
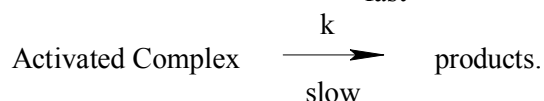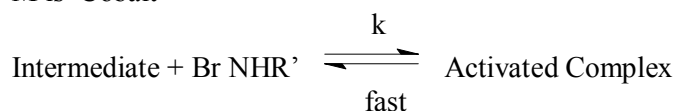
Mechanism

$$R-\underset{\underset{O}{||}}{C}-NH_2 + M^{n+} \rightleftharpoons R-\underset{\underset{O-M}{|}}{C}=\overset{+}{N}H_2 + M^{(n+ -1)}$$

M is metal silver, cobalt.   Intermediate

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

Activated complex

$$R-\underset{\underset{O-M}{|}}{C}=\overset{+}{N}H_2 \quad Br^-+NHR' + H_2O \xrightarrow[rds]{Slow} R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-\overset{+}{N}H_2 \ Br^- + R'NH^- + M^{n+}$$

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

Conventional reaction scheme may be formulated as under:

$$\text{Amide} + M^{n+} \xrightarrow{k} \text{Intermediate (fast)}$$

M is Cobalt

$$\text{Intermediate} + Br \, NHR' \xrightarrow[fast]{k} \text{Activated Complex}$$

$$\text{Activated Complex} \xrightarrow[slow]{k} \text{products.}$$
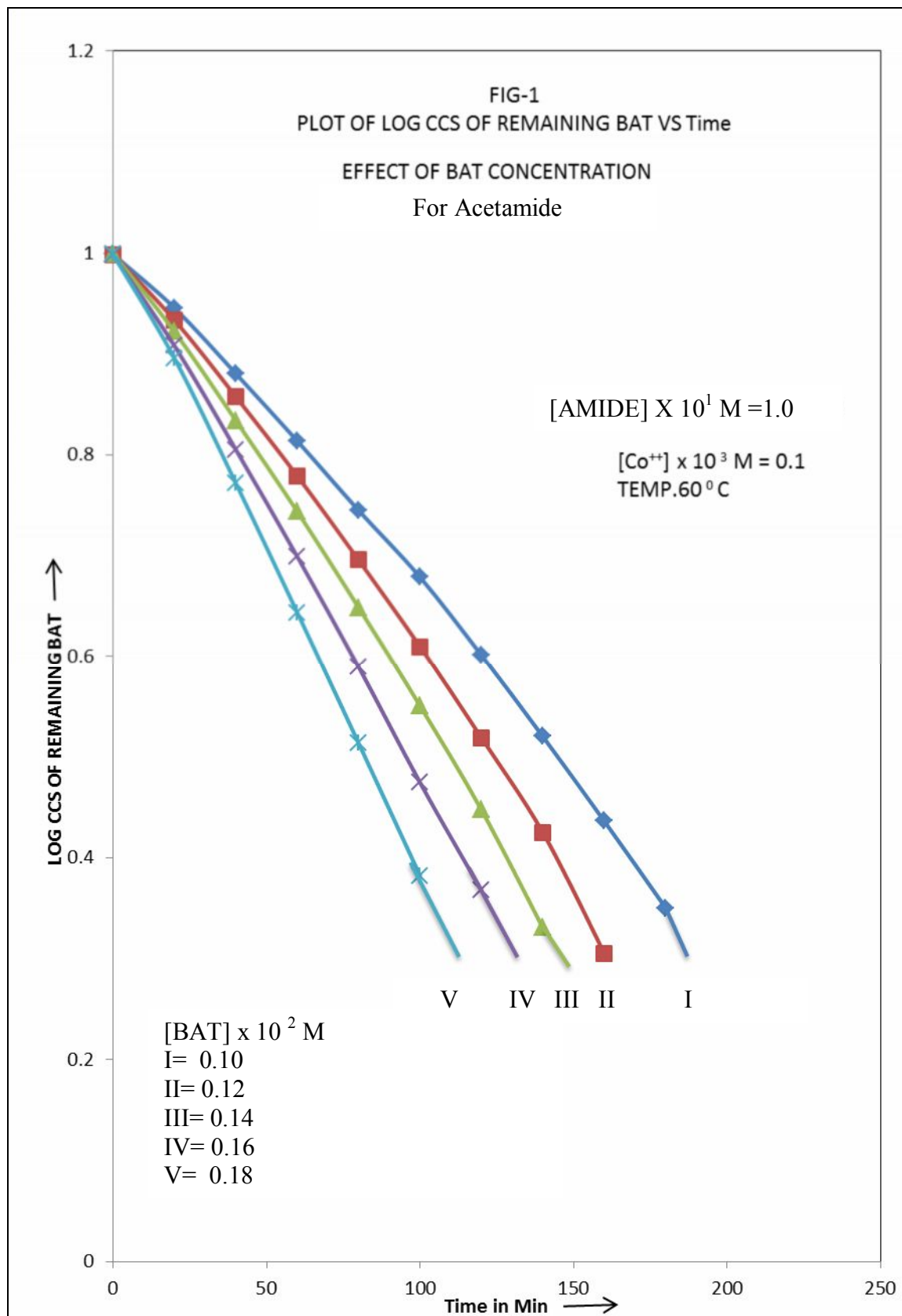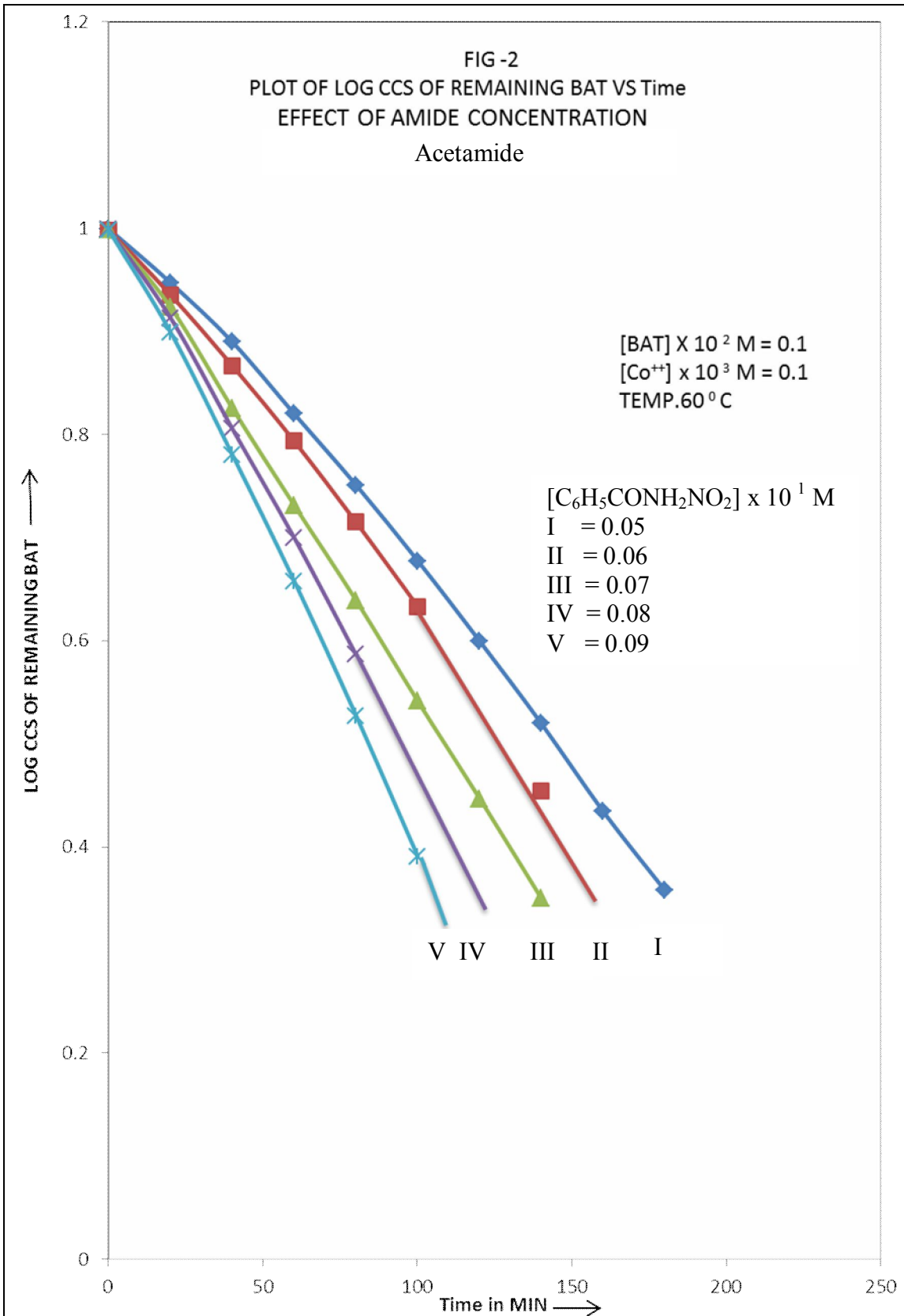
The following rate equation may be derived for the above mechanism in terms of consumption of BAT.

Rate = k (activated complex) (H$_2$O) 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.

FIG-1
PLOT OF LOG CCS OF REMAINING BAT VS Time

EFFECT OF BAT CONCENTRATION

For Acetamide

[AMIDE] X 10^1 M =1.0

[Co^{++}] x 10^3 M = 0.1
TEMP.60^0 C

V   IV   III   II   I

[BAT] x 10^2 M
I= 0.10
II= 0.12
III= 0.14
IV= 0.16
V= 0.18

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FIG -2
PLOT OF LOG CCS OF REMAINING BAT VS Time
EFFECT OF AMIDE CONCENTRATION
Acetamide

[BAT] X 10^2 M = 0.1
[Co^{++}] x 10^3 M = 0.1
TEMP.60^0 C

[$C_6H_5CONH_2NO_2$] x 10^1 M
I   = 0.05
II   = 0.06
III = 0.07
IV = 0.08
V   = 0.09

FIG -3

PLOT OF k x 10³ min⁻¹ vs [Co⁺⁺] x 10³ M

Uncatalysed reaction is possible

For Acetamide

[BAT] X 10^2 M =1.0
[AMIDE] X 10^1 M = 1.0

III 65 °C

II 60 °C

I 55 °C

k x 10³ min⁻¹

[Co⁺⁺ x 10³ M →

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