

KINETICS OF OXIDATION OF ALIPHATIC PRIMARY AMINES BY CAB IN ALKALINE MEDIUM CATALYZED BY β -CYCLODEXTRINE

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ABSTRACT

Kinetics of oxidation of a typical aliphatic primary amines namely n-propyl amine (nPA) and n-butyl amine (nBA) by Chloramine-B (CAB) has been studied in alkaline medium using β -Cyclodextrine (β CD) as catalyst at 50 °C. The rate shows first order dependence of rate on CAB and zero order dependence of rate on both [amine] which tends to fractional order dependence of rate on catalyst was observed, when $[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$. The reaction is almost independent of $[\text{OH}^-]$ and other effects, like chloride, sulphate ions, Benzenesulphonamide (BSA). Effect of ionic strength and dielectric constant of medium has also been studied. The reaction has been studied at different temperatures and a mechanism conforming to the kinetic observations is suggested.

Keywords: Kinetics, Oxidation, Amines, CAB, β -Cyclodextrine

INTRODUCTION

Considerable attention has centered around the chemistry of *N*-metallo-*N*-arylhalosulphonamides generally known as organic halomines, because of their versatility in behaving as mild oxidants, halogenting agents and *N*-anions, which act as both bases and nucleophilic. The important chlorine compound Chloramine-T (CAT), which is a byproduct during saccharin manufacture, is well known as an analytical reagent for the determination of diverse substrates. Mechanistic aspects of many of these reactions have been documented¹⁻³. The benzene analogue sodium *N*-chlorobenzenesulphonamide ($\text{C}_6\text{H}_5\text{SO}_2\text{NCINa} \cdot 1.5\text{H}_2\text{O}$) or (CAB) is becoming important as a mild oxidant^{4,5} and the compound can be easily prepared from benzenesulphonamide and chlorine.

Some kinetics studies of reactions of aromatic amines and their derivatives with chloramines-T (CAT) have been reported by Ramaiah and Rao⁶ and Radhakrishnamurthy and Rao⁷. These investigations have shown that the aromatic amine oxidations are independent of changing $[\text{OH}^-]$. Gupta and Agrawal have found that the kinetics of *s*-butylamine oxidation by CAT shows a retarding effect of alkali⁸. However, there is no information available in the literature on the kinetics of oxidation of aliphatic primary amines by Chloramine-B in presence of β CD. The present articles reports our studies on the kinetics of oxidation of two aliphatic primary amines viz. n-propylamine (nPA) and n-butylamine (nBA) catalyzed by β -Cyclodextrine in Chloramine-B.

Experimental

In a typical experiment, appropriate amount of primary amines, alkali, sodium perchlorate solution and water were taken in a reaction vessel and thermostated at desired temperature (30-60 °C) for thermal equilibrium. A measured amount of oxidant solution (CAB) also thermostated at same temperature was rapidly added in to the mixture which is in the reaction vessel.

The progress of the reaction was monitored by iodometric determination of unreacted oxidant in measured aliquot of the reaction mixture at different intervals of time. This was done by pipetting 5ml aliquot of the reaction mixture at regular intervals and run into conical flask containing quenching mixture (Ice cold mixture of 10ml of 10% KI, 10ml of 2N H_2SO_4 and 50ml of ice cold water).

The liberated iodine was than titrated against standard sodium thiosulphate, using starch as internal indicator near the end

point. The course of the reaction was followed for two half lives. The titer at $t = 0$ gives the value of 'a' the titer at any instant of time denotes (a-x).

Plot of $\log (a-x)$ ($\log [\text{oxidant}]$) vs time; or $\log V_0/v$ vs time were made. The values of pseudo first order rate constants k' obtained were reproducible within $\pm 3\%$. Regression analysis of the experimental data to obtain regression co-efficient 'r' was carried out on a CASIO fx-991ES scientific calculator.

MATERIAL AND METHODS

CAB was prepared as reported previously^{4,9}. An aqueous solution was prepared, standardized iodometrically and stored in brown bottle to prevent its photochemical degradation. Amines (Aldrich) were of accepted grades of purity and were used without further purification. All other reagents were of analytical grade. Doubly distilled water was employed in the preparation of aqueous solutions. The ionic strength of the system was maintained at a constant high value using concentrated solution of NaClO₄.

Product analysis

The reaction products of the amines, in the reaction mixture were detected by preparing their 2-4-dinitrophenylhydrazone derivatives, and by using Tollen's reagent test and chromic acid test¹⁰. (DNP derivatives of propionaldehyde, mp. 153.3 °C observed and 155 °C lit.¹¹, n-butylaldehyde, mp. 122 °C observed and 123 °C lit.¹²).

The other product ammonia was quantitatively estimated by the standard micro-Kjeldahl procedure. The reduced product of CAB, benzene sulphonamide was identified by paper chromatography using benzyl alcohol saturated with water as the solvent system and 0.5% vanillin in 1% HCl in EtOH as the visualizing reagent ($R_f = 0.905$).

RESULTS

Effect of reactants on the rate of reaction

The kinetic run was carried out with stoichiometric excess of substrate at constant $[\text{NaOH}]$ and $[\beta\text{CD}]$, Plots of $\log [\text{CAB}]$ vs time were linear with slope equal to unity table-1, fig.1 indicating first order dependence of the reaction rate on $[\text{CAB}]$. The value of pseudo first order rate constant 'k' is given in table-2 under the same experimental conditions. An increase in $[\text{amine}]$ has no effect on the rate, thus indicating zero - order dependence on $[\text{amines}]$ table -3.

Table 1: Rate of primary amines of oxidation by CAB

nPA	nBA
Time (min)	log [CAB]
0	1.198
10	1.017
15	0.939
20	0.851
25	0.763
30	0.672
40	0.505
50	0.230
r	0.9924
k	$6.397 \times 10^{-4} \text{ sec}^{-1}$

[CAB] = $5 \times 10^{-3} \text{ mol dm}^{-3}$, [Amine] = $10 \times 10^{-2} \text{ mol dm}^{-3}$, [NaOH] = $5 \times 10^{-2} \text{ mol dm}^{-3}$,

[β CD] = $5 \times 10^{-3} \text{ mol dm}^{-3}$ and T = 323K

Table 2: Effect of varying [CAB] on the rate of reaction of primary amines

10^3 [CAB] mol dm ⁻³	10^4 k sec ⁻¹ nPA nBA
1.0	6.30 7.25
3.0	6.38 7.27
5.0	6.39 7.22
7.0	6.35 7.21
9.0	6.38 7.21

[Amine] = $10 \times 10^{-2} \text{ mol dm}^{-3}$, [NaOH] = $5 \times 10^{-3} \text{ mol dm}^{-3}$,

[β CD] = $5 \times 10^{-3} \text{ mol dm}^{-3}$ and T = 323K

Table 3: Effect of varying [amine] on the rate of oxidation by CAB

10^2 [Amine] mol dm ⁻³	10^4 k sec ⁻¹ nPA nBA
2.5	6.40 7.19
7.5	6.38 7.21
10.0	6.39 7.22
15.0	6.35 7.16
30.0	6.43 7.15

[CAB] = $5 \times 10^{-3} \text{ mol dm}^{-3}$, [NaOH] = $5 \times 10^{-2} \text{ mol dm}^{-3}$, [β CD] = $5 \times 10^{-3} \text{ mol dm}^{-3}$ and T = 323K

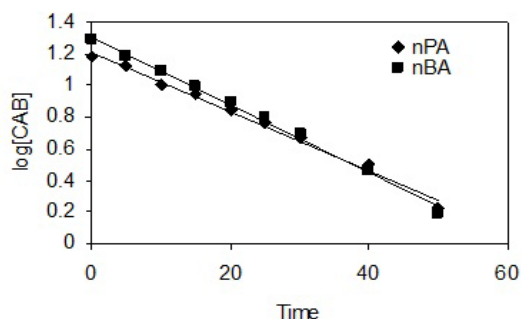


Fig. 1: Effect of concentration on rate of oxidation of primary amines by Chloramine-B

Effect of NaOH on the rate of reaction

At constant [CAB], [amines], [β CD] and temperature the rate increased with increase in [NaOH] ($1 \times 10^{-2} \text{ mol dm}^{-3}$ to $10 \times 10^{-2} \text{ mol dm}^{-3}$). The plots of $\log k$ vs $\log [\text{NaOH}]$ were linear with a slope less than unity (≈ 0.40) indicating fractional order dependence on [NaOH] table-4, fig.2.

Table 4: Effect of [NaOH] on the rate of oxidation of primary amines

10^2 [NaOH] mol dm ⁻³	10^4 k sec ⁻¹ nPA nBA
1.0	3.41 3.68
2.5	4.84 5.52
5.0	6.39 7.22
7.5	8.04 8.62
10.0	9.77 9.69

[Amine] = $10 \times 10^{-2} \text{ mol dm}^{-3}$, [CAB] = $5 \times 10^{-3} \text{ mol dm}^{-3}$,

[β CD] = $5 \times 10^{-3} \text{ mol dm}^{-3}$ and T = 323K

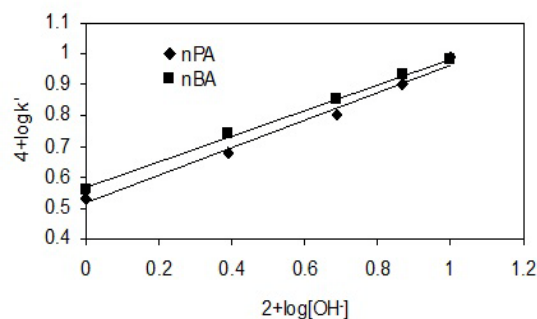


Fig. 2: Effect of [OH-] on the rate of reaction

Effect of β -Cyclodextrine on the rate of reaction

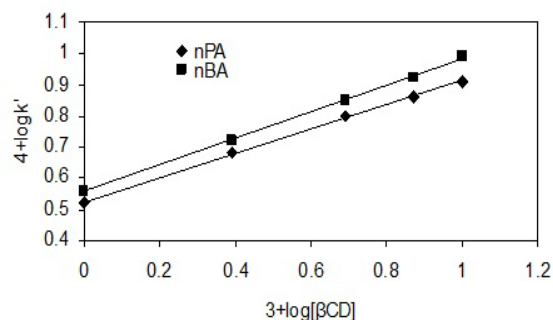
At constant [CAB], [amine], [NaOH] and temperature, the rate of a reaction increases with increase in [β CD] ($1 \times 10^{-3} \text{ mol dm}^{-3}$ to $10 \times 10^{-3} \text{ mol dm}^{-3}$). The plots of $\log k$ vs $\log [\beta\text{CD}]$ were linear with slope less than unity (≈ 0.40) indicating fractional order dependence on [β CD] table-5, fig.3.

Table 5: Effect of [β CD] on the rate of reaction of primary amines

10^3 [β CD] mol dm ⁻³	10^4 k sec ⁻¹ nPA nBA
1.0	3.32 3.65
2.5	4.82 5.33
5.0	6.39 7.22
7.5	7.34 8.43
10.0	8.18 9.85

[Amine] = $10 \times 10^{-2} \text{ mol dm}^{-3}$, [CAB] = $5 \times 10^{-3} \text{ mol dm}^{-3}$,

[NaOH] = $5 \times 10^{-2} \text{ mol dm}^{-3}$ and T = 323K

Fig. 3: Effect of [β CD] on the rate of reaction

Effect of [Cl⁻] ion on the rate of reaction:

Effect of [Cl⁻] was studied by adding NaCl to the reaction mixture (0.1 mol dm^{-3} to 0.5 mol dm^{-3}). It showed that the increase in [Cl⁻] has no effect on the rate of a reaction table -6.

Table 6: Effect of complexing agents on the rate constant for the oxidation of Primary amines by CAB

[NaCl] mol dm ⁻³	10 ⁴ k sec ⁻¹		
	nPA	nBA	
0.1	6.39	7.25	
0.2	6.36	7.19	
0.3	6.39	7.22	
0.4	6.35	7.14	
0.5	6.32	7.17	
10 ³ [BSA] mol dm ⁻³	10 ⁴ k sec ⁻¹		
	nPA	nBA	
	2	6.39	7.22
	4	6.34	7.19
6	6.38	7.28	
8	6.35	7.20	
[NaClO ₄] mol dm ⁻³	10 ⁴ k sec ⁻¹		
	nPA	nBA	
	0.0	6.39	7.22
	0.1	6.34	7.30
	0.2	6.33	7.23
	0.3	6.29	7.19
0.4	6.33	7.25	
0.5	6.38	7.25	

[Amine] = 10x10⁻² mol dm⁻³, [CAB] = 5x10⁻³ mol dm⁻³, [NaOH] = 5x10⁻² mol dm⁻³

[βCD] = 5x10⁻³ mol dm⁻³ and T = 323K

Effect of Benzenesulphonamide on the rate of reaction:

The addition of reaction product benzenesulphonamide[BSA] (2 x10⁻³ to 8 x 10⁻³ mol dm⁻³) has no effect on the rate of reaction table-6, indicating that it is not involved in pre-equilibrium to the rate - determining step table-10.

Table 10: Values of equilibrium and formation constant of primary amine -βCD Complex determined from the double reciprocal plot

Substrate	a	b	K ₂ (litre mole ⁻¹)	10 ³ k ₃
	10 ⁻³ K ₁	10 ⁻⁴ K ₁		
n-Propylamine	0.631	0.110	59.5	1.83
n-Butylamine	0.668	0.134	52.9	1.72

a) From double reciprocal plot of k¹ versus [βCD] at constant [OH⁻]

b) From double reciprocal plot of k¹ versus [OH⁻] at constant [βCD]

Effect of ionic strength on the rate of reaction:

Ionic strength of the medium was varied by adding NaClO₄ (0.1 mol dm⁻³ - 0.5 mol dm⁻³). It was seen that the variation of ionic strength has no effect on the rate of the reaction table -6.

Effect of dielectric constant of the medium on rate of reaction:

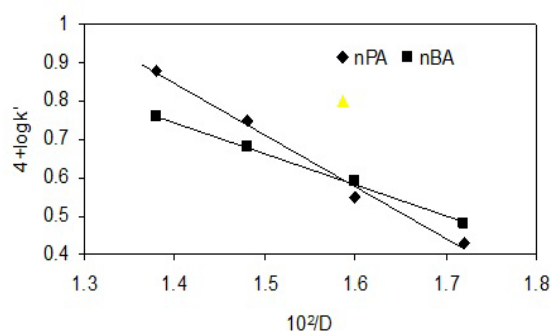
The reaction was studied in aqueous medium containing varied amounts of methanol 10 - 40% v/v). A decrease in the reaction rate was observed with increase in quantities of methanol. The plot of log k vs 1/D, where 'D' is dielectric constant of the medium is linear with negative slope table-7, fig.4. In blank experiment methanol was negligibly oxidized by CAB under these experimental conditions.

Table 7: Effect of dielectric constant(D) of the medium on the rate of reaction of primary amines

Methanol % (v/v)	D 10 ² /D	10 ⁴ k sec ⁻¹		
		nPA	nBA	
10	72.37	1.38	7.67	5.87
20	67.48	1.48	4.96	4.86
30	62.71	1.60	3.56	3.80
40	58.06	1.72	2.70	3.05

[Amine] = 10x10⁻² mol dm⁻³, [CAB] = 5x10⁻³ mol dm⁻³, [NaOH] = 5x10⁻² mol dm⁻³,

[βCD] = 5x10⁻³ mol dm⁻³ and T = 323 K

**Fig. 4: Effect of dielectric constant of the medium on the rate of reaction**

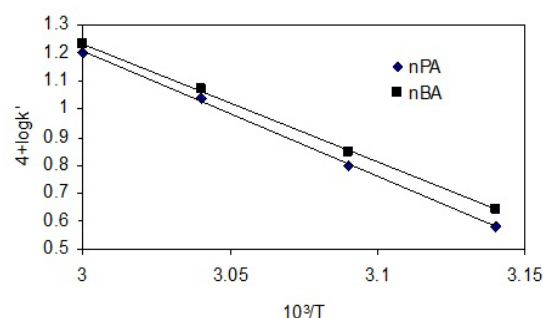
Effect of temperature on the rate of reaction

The reaction was studied at different temperatures in the range 318K - 333K and the value of 'k' were determined from the pseudo first order plot table-8, fig.5. The energy of activation 'E_a' was evaluated. The other activation parameters were calculated and are presented in table 9.

Table 8: Effect of temperature on the rate of reaction for the oxidation of primary amines by CAB in presence of β-Cyclodextrine catalyst

T/K	10 ⁴ k scc ⁻¹	
	nPA	nBA
318	3.89	4.45
323	6.39	7.22
328	10.98	11.93
333	15.89	17.34

[Amine] = 10x10⁻² mol dm⁻³, [CAB] = 5x10⁻³ mol dm⁻³, [NaOH] = 5x10⁻² mol dm⁻³ and [βCD] = 5x10⁻³ mol dm⁻³

**Fig. 5: Effect of temperature on the rate of reaction****Table 9: Activation parameters for the oxidation of primary amines by CAB in presence of β-Cyclodextrine catalyst**

T.D. Parameters	nPA	nBA
E _a kJ/mol	11.24	9.75
ΔH [#] kJ/mol	86.65	77.08
ΔS [#] JK ⁻¹ /mol	-36.49	-67.10
ΔG [#] kJ/mol	74.74	55.16

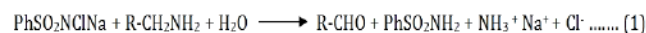
Test of free radicals on the rate of reaction:

The addition of reaction mixture to aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of *in situ* formation of free radical species in the reaction sequence.

Stoichiometry

Reaction mixtures containing varying ratio of oxidant to amines were equilibrated in 5 x 10⁻² mol dm⁻³ of NaOH and 5 x 10⁻³ mol dm⁻³

of β -Cyclodextrine at 323K for about 24 hours with $[\text{oxid}]_0 > [\text{S}]_0$. The excess unreacted oxidant was estimated by iodometric titration with standard sodium thiosulphate. It was found that one mole of substrate consumed one mole of the oxidant to yield the corresponding aldehyde, conforming to equation (1).

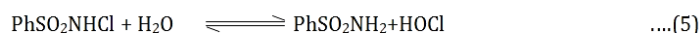
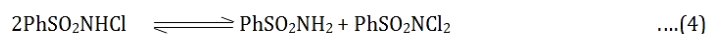
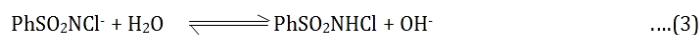
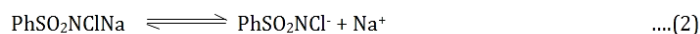


R= CH_3CH_2 for n-propyl amine

$\text{CH}_3\text{CH}_2\text{CH}_2$ for n-butyl amine

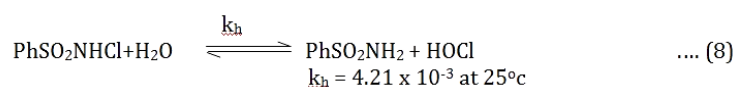
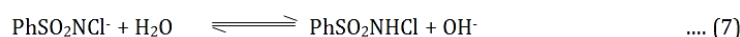
DISCUSSION

Pryde and Soper¹³, Morris et al.¹⁴ and Bishop and Jennings¹⁵ have showed that the existence of similar equilibrium in acid/alkaline solution of N-metallo-N-haloaryl sulphonamide. CAB analogous to CAT, behaves as a strong electrolyte in aqueous solution, forming different species as shown in equation 2- 6.

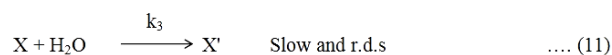
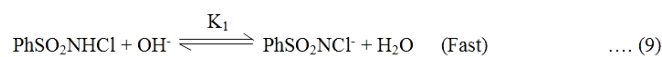


In acidic medium the probable oxidizing species are free acid PhSO_2NHCl , $\text{PhSO}_2\text{NCl}_2$, HOCl and H_2OCl^+ . In the medium, where $\text{PhSO}_2\text{NCl}_2$ and H_2OCl^+ do not exist, the expected reactive species

are PhSO_2NHCl , HOCl and $\text{PhSO}_2\text{NCl}_2$. Hardy and Johnston¹⁶ have reported the existence of following equilibrium in alkaline solution of CAB.



As equation (8) indicates a slow hydrolysis, if HOCl is the primary oxidizing species, a first retardation of the rate by the added BSA would be expected, which was not observed. If PhSO_2NHCl were the reactive species, a retardation of the rate by $[\text{OH}^-]$ would be expected (eq.7), which has also not been observed. Therefore it is likely that the anion $\text{PhSO}_2\text{NCl}^-$ itself acts as the reactive species responsible for the oxidation of amines. The following Scheme -1 is therefore proposed to explain the experimentally observed reaction.



SCHEME 1

Where 'S' is primary amines (nPA or nBA) and X and X' are the intermediate complexes. From the above scheme

$$[\text{CAB}]_t = [\text{PhSO}_2\text{NHCl}] + [\text{PhSO}_2\text{NCl}^-] + [\text{X}] \dots(13)$$

We can write from equations (9) and (10),

$$[\text{PhSO}_2\text{NCl}^-] = \frac{[\text{X}]}{K_2 [\beta\text{CD}]} \dots(14)$$

$$\text{And } [\text{PhSO}_2\text{NHCl}] = \frac{[\text{X}]}{K_2[\beta\text{CD}]} \frac{[\text{H}_2\text{O}]}{K_1[\text{OH}^-]} \dots(15)$$

By substituting for $[\text{PhSO}_2\text{NCl}^-]$ and $[\text{PhSO}_2\text{NHCl}]$ in equation (13) and rearranging we have.

$$[\text{X}] = \frac{K_1 K_2 [\beta\text{CD}] [\text{OH}^-] [\text{CAB}]_t}{[\text{H}_2\text{O}] + K_{-1} [\text{OH}^-] + K_1 K_2 [\beta\text{CD}] [\text{OH}^-]} \dots(16)$$

$$\text{Since rate} = k_3 [\text{X}] [\text{H}_2\text{O}] \dots(17)$$

On substituting equation (16) in (17)

$$\text{rate} = \frac{d[\text{CAB}]_t}{dt} = \frac{k_3 K_2 K_1 [\beta\text{CD}] [\text{OH}^-][\text{CAB}]_t[\text{H}_2\text{O}]}{K_1[\text{OH}^-] + K_1 K_2 [\beta\text{CD}] + [\text{H}_2\text{O}]} \quad \dots (18)$$

The above rate law is in agreement with experimental data, which includes first order

in $[\text{CAB}]$, fractional order in $[\beta\text{CD}]$ and $[\text{OH}^-]$.

$$\text{Experimentally rate} = k'[\text{CAB}]_t \quad \dots (19)$$

$$\text{Therefore } k' = \frac{k_3 K_2 K_1 [\beta\text{CD}] [\text{OH}^-][\text{H}_2\text{O}]}{K_1[\text{OH}^-] + K_1 K_2 [\beta\text{CD}] + [\text{H}_2\text{O}]} \quad \dots (20)$$

Taking reciprocal equation (20) can be written as

$$\frac{1}{k'} = \frac{1}{k_3 K_2 [\beta\text{CD}]} + \frac{1}{k_3 [\text{OH}^-]} + \frac{1}{k_3 K_2 K_1 [\beta\text{CD}] [\text{OH}^-]} \quad \dots (21)$$

Where, $(k'_3 = k_3[\text{H}_2\text{O}])$

$$\text{Therefore } \frac{1}{k'} = \frac{1}{[\beta\text{CD}]} \left\{ \frac{1}{k'_3 K_2} + \frac{1}{k'_3 K_2 K_1 [\text{OH}^-]} \right\} + \frac{1}{k'_3 [\text{OH}^-]} \quad \dots (22)$$

On rearranging equation (21) it can be written as

$$\frac{1}{k'} = \frac{1}{[\text{OH}^-]} \left\{ \frac{1}{k'_3 K_2 K_1 [\beta\text{CD}]} + \frac{1}{k'_3} \right\} + \left\{ \frac{1}{k'_3 K_2 [\beta\text{CD}]} \right\}$$

A Plot of $1/k'$ vs $1/[\beta\text{CD}]$ and $1/k'$ vs $1/[\text{OH}^-]$ is found to be linear.

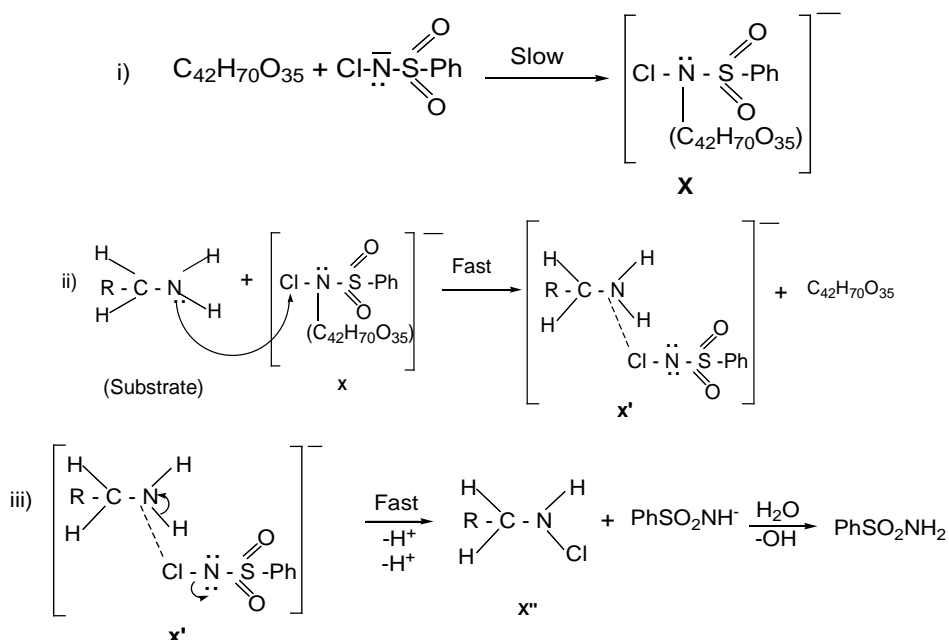
From the slope and intercept of the plots the values of k_3 , K_2 and K_1 are calculated (table -10). The fairly constant values of K_1 and K_2 for the step (9) and (10) respectively indicates that proposed Scheme 1 is correct.

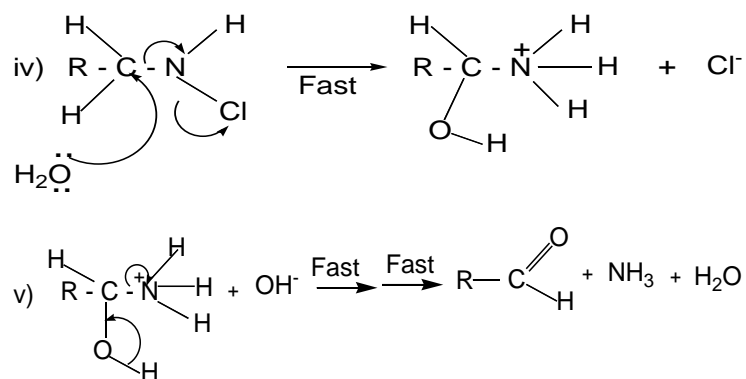
Fairly large value ΔG^\ddagger indicates that the activated complex is solvated as is given by the slow r.d.s step (eq.11) in Scheme 1. A negative ΔS^\ddagger indicates an ordered activated complex. The decrease in the rate constant with decreasing constant also supports this view in Scheme II.

A detailed mechanistic interpretation of βCD catalyzed oxidation of the primary amines by CAB in NaOH medium is presented in Scheme II. An anion of the oxidizing species, $(\text{PhSO}_2\text{NCl})^-$

coordinates through the sulphonamide nitrogen atom to activate CAB by stabilizing the charge on its nitrogen atom and polarizing the N-Cl bond in the complex species X in the slow step (step i). In the fast step ii, an electrophilic attack by the positive chlorine of the complex X at the amino nitrogen of the substrate forms the intermediate complex species X' and regenerate the catalyst βCD .

In the next fast step iii, the intermediate X' disproportionates into an N-chloramine species X'' and $(\text{PhSO}_2\text{NCH})^-$ which on hydrolysis can form the reduction product PhSO_2NH_2 . The step iv involves a nucleophilic attack by H_2O , followed by intramolecular rearrangements, forming an N-protonated amine intermediate is attacked by OH^- to form the aldehyde, NH_3 and H_2O .





Here, Ph = C₆H₅ and R = CH₃CH₂ for nPA, CH₃CH₂CH₂ for nBA.

SCHEME II

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