

**KINETICS OF OXIDATION OF ETHYLAMINE,
MONOETHANOLAMINE AND BENZYLAMINE
BY CHLORAMINE-T**

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ABSTRACT

The kinetics and mechanism of oxidation of ethylamine, benzylamine and monoethanolamine by chloramine-T in alkaline medium have been investigated, the solvent system being aqueous and aqueous-ethanolic medium. The reactions are first order in chloramine-T, fractional order in benzylamine and monoethanolamine, fractional order at 0.22 M NaOH but zero order at lower alkali, i.e 0.055 M NaOH in ethylamine. There is an increase in the rate with the increase in alkali, initially in the range 0.0011 M up to 0.011 M alkali with monoethanolamine and benzylamine, beyond which the rate decreases with the increase in alkali. In the case of ethylamine the reaction rate increases initially and appears to be independent beyond $0.022 \text{ mol dm}^{-3}$ of alkali concentration. pH profile of all the compounds between zero to 6.85 and 6.85 to 14 has been studied. Catalysis has been observed in the case of monoethanolamine with Os(VIII) and Ru(III). There is no effect of Ru(III) whereas there is a minimum increase in the rate with Os(VIII) for benzylamine and ethylamine, a two fold rate increase for sixty fold increase in the case of Os(VIII) which can be traced to be salt effect. All the kinetic features have been explained by postulating a suitable mechanism and rate law.

Keywords: kinetics, oxidation, ethylamine, monoethanolamine, benzylamine, chloramine-T.

AIMS AND BACKGROUND

Considerable work has been reported on the oxidation of substituted aliphatic alcohols like ethanolamine by chloramine-T (Ref. 1), bromamine-T (Ref. 2) and N-bromosuccinimide³. A perusal of the reported work does not make it clear whether the site of oxidation is the amino group or the hydroxyl group in the rate-determining step. Hence, it was thought worthwhile to investigate thoroughly the oxidation of ethanolamine by chloramine-T in alkaline medium both in uncatalyzed and catalyzed conditions with Os(VIII) and Ru(III).

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EXPERIMENTAL

The substrates used were ethylamine, benzylamine and monoethanolamine and the catalysts— RuCl_3 and OsO_4 . All the reagents used were of analytical reagent grade.

Kinetics was followed by estimating chloramine-T iodometrically at various intervals of time.

The primary products were the corresponding aldehydes from ethylamine and benzylamine whereas it was the corresponding amino aldehyde for ethanolamine.

RESULTS AND DISCUSSION

The relevant kinetic data under uncatalyzed conditions is given in Tables 1A, 1B and 1C. The reactions are first order in chloramine-T, fractional order in ethanolamine. Initially the rate increases in alkali concentration up to $0.055 \text{ mol dm}^{-3}$ and later decreases with the increase in concentration showing inverse fractional order in alkali. The initial direct fractional dependence of alkali and later the inverse fractional dependence can be explained by postulating the

Table 1A. Oxidation of ethylamine by chloramine-T in alkali medium
 $[\text{CAT}] = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{ethylamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{OH}^-] = 5.5 \times 10^{-2} \text{ mol dm}^{-3}$;
 temperature 40°C

Variant	Concentration of variant	$k_1 \times 10^4 \text{ (min}^{-1}\text{)}$
CAT	$7.5 \times 10^{-4} \text{ mol dm}^{-3}$	25.38
	$15.0 \times 10^{-4} \text{ mol dm}^{-3}$	30.22
	$22.5 \times 10^{-4} \text{ mol dm}^{-3}$	29.83
Ethylamine at $5.5 \times 10^{-2} \text{ mol dm}^{-3}$	$0.625 \times 10^{-2} \text{ mol dm}^{-3}$	27.74
	$1.25 \times 10^{-2} \text{ mol dm}^{-3}$	31.10
	$2.50 \times 10^{-2} \text{ mol dm}^{-3}$	32.99
	$5.00 \times 10^{-2} \text{ mol dm}^{-3}$	25.38
Ethylamine at $22.0 \times 10^{-2} \text{ mol dm}^{-3}$	$5.00 \times 10^{-2} \text{ mol dm}^{-3}$	60.10
	$10.00 \times 10^{-2} \text{ mol dm}^{-3}$	86.10
	$20.00 \times 10^{-2} \text{ mol dm}^{-3}$	142.15
	$40.00 \times 10^{-2} \text{ mol dm}^{-3}$	182.09
OH^-	$5.5 \times 10^{-2} \text{ mol dm}^{-3}$	25.38
	$11.00 \times 10^{-2} \text{ mol dm}^{-3}$	49.47
	$22.00 \times 10^{-2} \text{ mol dm}^{-3}$	60.10
	$49.46 \times 10^{-2} \text{ mol dm}^{-3}$	60.54
	$93.22 \times 10^{-2} \text{ mol dm}^{-3}$	60.26
EtOH	0 %	25.38
	10 %	145.41
	20 %	122.57
	40 %	90.61
	60 %	53.61
Temperature	40°C	25.38
	50°C	89.28
	60°C	200.58

Table 1C. Oxidation of ethanalamine by chloramine-T [CAT] = 7.5×10^{-4} mol dm⁻³; [ethanalamine] = 5.0×10^{-2} mol dm⁻³; [OH⁻] = 5.5×10^{-2} mol dm⁻³; temperature 40°C

Variant	Concentration of variant	$k_1 \times 10^4$ (min ⁻¹)
CAT	3.75×10^{-4} mol dm ⁻³	54.91
	7.5×10^{-4} mol dm ⁻³	53.56
	15.0×10^{-4} mol dm ⁻³	54.44
	22.5×10^{-4} mol dm ⁻³	51.87
Ethanalamine	0.625×10^{-2} mol dm ⁻³	16.13
	1.25×10^{-2} mol dm ⁻³	24.47
	2.50×10^{-2} mol dm ⁻³	45.01
	5.00×10^{-2} mol dm ⁻³	53.56
	10.00×10^{-2} mol dm ⁻³	63.37
	20.00×10^{-2} mol dm ⁻³	69.37
OH ⁻	40.00×10^{-2} mol dm ⁻³	90.49
	0.55×10^{-2} mol dm ⁻³	34.15
	1.10×10^{-2} mol dm ⁻³	36.26
	5.50×10^{-2} mol dm ⁻³	53.56
	11.00×10^{-2} mol dm ⁻³	41.69
	22.00×10^{-2} mol dm ⁻³	28.29
EtOH	44.00×10^{-2} mol dm ⁻³	22.00
	90.00×10^{-2} mol dm ⁻³	20.15
	0 %	53.56
Temperature	20 %	33.59
	40 %	22.38
	60°C	244.75

$$(\text{CAT})_T = \text{CAT} + \text{CAT}' + C_1 + C_2 = \text{CAT} \left\{ 1 + \frac{K}{[\text{OH}^-]} + \frac{KK_1S}{[\text{OH}^-]} + K_2S \right\}$$

$$= \frac{\text{CAT}}{[\text{OH}^-]} \{ [\text{OH}^-] + K + KK_1S + K_2S \}$$

$$\text{rate} = k_1 C_1 + k_2 C_2 = \frac{k_1 KK_1 [\text{CAT}] [S]}{[\text{OH}^-]} + k_2 K_2 [\text{CAT}] [S]$$

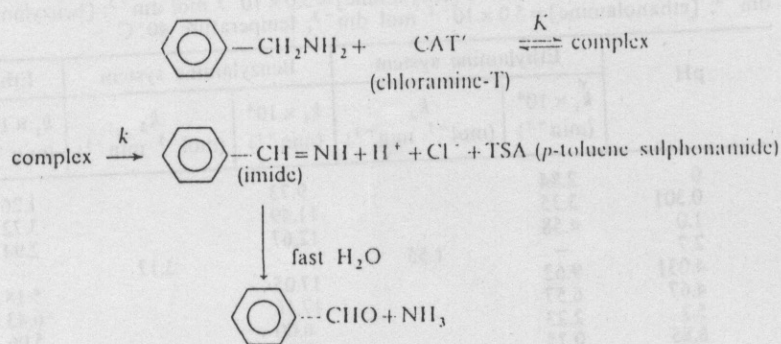
$$= \frac{k_1 KK_1 [\text{CAT}]_T [S] + k_2 K_2 [\text{CAT}]_T [S] [\text{OH}^-]}{[\text{OH}^-] + K + KK_1S + K_2S [\text{OH}^-]} = \frac{[\text{CAT}]_T [S] \{ k_1 KK_1 + k_2 K_2 [\text{OH}^-] \}}{[\text{OH}^-] + K + KK_1S + K_2S [\text{OH}^-]}$$

The rate law explains the observed orders of: first order in oxidant, fractional order in substrate, initial direct dependence and later inverse fractional order of hydroxide for benzylamine and ethanalamine and initial direct dependence at lower alkali and later independence to alkali for ethylamine. The zero order of ethylamine at low concentration of alkali at $0.055 \text{ mol dm}^{-3}$ can also be explained by the above rate law.

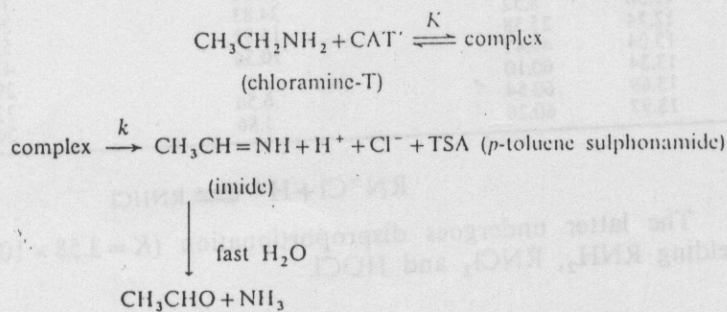
The following sequence will represent the oxidation process:

Mechanism of the reaction process

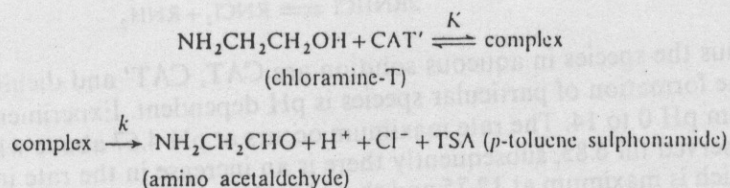
a.



b.



c.



In summary the kinetic orders observed are as follows: first order in oxidant, fractional order in substrate at the alkali concentration studied for ethylamine, benzylamine and ethanolamine, direct fractional order of alkali which becomes inverse fractional order at higher alkali concentration for benzylamine and ethanolamine, and independence to alkali at higher concentration for ethylamine and the zero order nature of ethylamine at lower alkali concentration which becomes fractional order at higher alkali concentration.

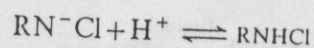
pH Profile. According to Bishop and Jennings⁴, CAT is a strong electrolyte in aqueous solution and dissociates as



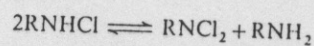
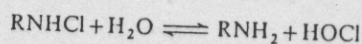
The free acid form becomes RNHCl by taking a proton

Table 2. pH Profile. Oxidation of ethylamine, benzylamine and ethanolamine by chloramine-T
 $[CAT] = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{ethylamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{benzylamine}] = 0.6 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{ethanolamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; temperature 40°C

pH	Ethylamine system		Benzylamine system		Ethanolamine system	
	$k_1 \times 10^4$ (min^{-1})	k_2 ($\text{mol}^{-1} \text{min}^{-1}$)	$k_1 \times 10^4$ (min^{-1})	k_2 ($\text{mol}^{-1} \text{min}^{-1}$)	$k_1 \times 10^4$ (min^{-1})	k_2 ($\text{mol}^{-1} \text{min}^{-1}$)
0	2.84		9.73		1.26	
0.301	3.35		11.49		3.72	
1.0	4.58		12.67		2.94	
2.7	—	1.55	—	3.17	—	3.77
4.031	9.62		17.05		—	
4.67	6.57		17.16		5.18	
5.3	2.23		6.00		6.43	
6.85	0.75		2.95		5.06	
8.9	2.54		9.16		3.59	
10.00	3.72		12.06		9.85	
11.50	8.52		34.83		16.67	
12.74	25.38		15.82		28.37	
13.04	49.47		10.36		53.56	
13.34	60.10		—		41.69	
13.69	60.54		6.56		29.73	
13.97	60.26		5.86		23.58	
					20.15	

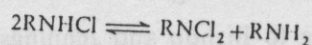


The latter undergoes disproportionation ($K = 3.58 \times 10^{-4}$) or hydrolysis yielding RNH_2 , RNCl_2 and HOCl .



Thus the species in aqueous solution are CAT, CAT' and dichloramine-T (DCT). The formation of particular species is pH dependent. Experiments are carried out from pH 0 to 14. The rate maximum occurs at pH 4.67 above which retardation is observed till 6.85, subsequently there is an increase in the rate in the alkali region which is maximum at 12.75 and there is a decrease in the rate with further increase in pH.

The variation of CAT concentration has been done at different pH levels to determine the nature of CAT species present at a particular pH. The observation is: there is a first order dependence on CAT in the pH range from 0 to 2.4 where RNCl_2 ion is the active species. There is a second order dependence on CAT between pH 2.7 to 3.5 showing the existence of DCT in this pH range. According to equilibrium:



The plots of $1/\text{CAT}$ versus time are linear and there is a fair constancy in the second order constant with respect to CAT. The existence of DCT at pH 3.5 has been reported earlier by Radhakrishnamurti and Panda⁵. At pH 4.67 the rate is maximum and the dependence on CAT is unity. The species is HOCl at this pH and this collaborated with the work of Mushran et al.⁶ The reaction rate

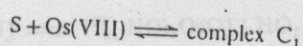
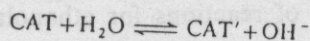
decreases till pH 6.85 and the dependence is first order on CAT. Hence, the species in the acid range of pH from zero to 6.85 are HOCl, DCT and RNCl. The reactivity order of these species is HOCl > DCT > RNHCl. In the alkaline range obviously the species is sodium salt till the pH of 12.74 after which the reverse equilibrium takes place giving CAT and sodium salts as mixed active species and there is observance of fractional order on OH⁻ concentration beyond pH 12.74. The relevant data is presented in Table 2.

Effect of solvent. Experiments have been conducted at different concentrations of ethanol. The rate decreases with the increase in percentage of ethanol indicating that these reactions are facilitated at a medium of high dielectric constant like water.

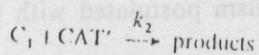
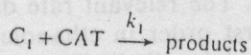
Catalyzed reactions. Ethanolamine. The object of the study is to fix the site of oxidation whether it is the amino group or the hydroxyl group. Experiments have been conducted with OsO₄ and Ru(III)Cl₃. It is well known that alcohols are well catalyzed by Ru(III) and OsO₄ in alkaline medium. Hence, for the purpose of comparison benzylamine has been subjected to oxidation by Ru(III) and OsO₄ in the presence of oxidant. It has been observed that there is no catalysis with Ru(III) and even with OsO₄ virtually the catalysis is minimum as in the concentration range of 0.16 × 10⁻⁵ to 9.6 × 10⁻⁵ mol dm⁻³ of Os(VIII) the rate increase is about twice for increase in concentration of the catalyst of sixty times. This might be due to catalysis but due to its functioning as a general salt adding to the ionic strength of the medium. But when ethanolamine is subjected to catalysis by Ru(III) and OsO₄ there is a perfect catalysis showing 0.5 order on Os(VIII) and 0.5 order on Ru(III). These facts put together indicate that the amino group is not much affected either by Os(VIII) or Ru(III) but it is the -OH group that participates by interaction either with Ru(III) or OsO₄ forming complexes which are decomposed by CAT in the rate-determining step.

Catalysis with Os(VIII). The relevant data for Os(VIII) catalyzed oxidation of ethanolamine by CAT is given in Table 3. The reactions are first order in CAT, first order in ethanolamine, fractional order in Os(VIII) and inverse fractional order on alkali. The reaction rate is visualized as follows:

Substrate complexes with OsO₄ which later reacts with CAT and CAT' to form the products in a rate-determining step. The corresponding rate law and mechanism are given below:



$$\text{CAT}' = \frac{K_1 [\text{CAT}]}{[\text{OH}^-]}$$



$$S_T = S + C_1 = S + K_2 S [\text{Os(VIII)}] = S \{1 + K_2 [\text{Os(VIII)}]\}$$

Table 3. Os(VIII) catalyzed oxidation of ethanolamine by chloramine-T
 [CAT] = 7.5×10^{-4} mol dm $^{-3}$; [ethanolamine] = 5.0×10^{-2} mol dm $^{-3}$; [Os(VIII)] = 7.6×10^{-5} mol dm $^{-3}$; [Ru(III)] = 19.0×10^{-5} mol dm $^{-3}$; [OH $^{-}$] = 22.0×10^{-2} mol dm $^{-3}$; temperature 40°C

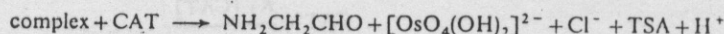
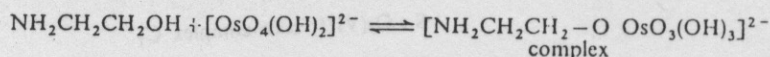
Variant	Concentration of variant (mol dm $^{-3}$)	$k_1 \times 10^4$ (min $^{-1}$) catalyst: Os(VIII)	$k_1 \times 10^4$ (min $^{-1}$) catalyst: Ru(III)
CAT	3.75×10^{-4}	52.86	46.67
	5.0×10^{-4}	—	42.97
	7.5×10^{-4}	51.00	50.00
	15.0×10^{-4}	50.22	48.32
Ethanolamine	1.25×10^{-2}	15.56	8.99
	2.50×10^{-2}	27.48	14.71
	5.00×10^{-2}	51.00	50.00
	10.00×10^{-2}	60.46	49.65
OH $^{-}$	11.00×10^{-2}	53.98	—
	22.00×10^{-2}	51.00	50.00
	44.00×10^{-2}	40.35	32.75
	66.00×10^{-2}	34.21	24.51
	75.00×10^{-2}	32.01	—
Os(VIII)	0	—	17.77
	0	28.29	—
	4.80×10^{-5}	37.69	—
	7.60×10^{-5}	51.00	—
	14.40×10^{-5}	70.94	—
Ru(III)	22.40×10^{-5}	121.13	—
	0	—	28.29
	7.6×10^{-5}	—	34.97
	13.3×10^{-5}	—	46.83
	19.0×10^{-5}	—	50.00
	28.5×10^{-5}	—	61.76

$$\text{rate} = k_1 C_1 \text{CAT} + k_2 C_1 \text{CAT}' = K_2 S \text{Os(VIII)} [\text{CAT}] \left\{ k_1 + \frac{k_2 K_1}{[\text{OH}^-]} \right\}$$

$$= \frac{K_2 S_T \text{Os(VIII)} [\text{CAT}]}{1 + K_2 \text{Os(VIII)} [\text{OH}^-]} \{ k_1 [\text{OH}^-] + k_2 K_1 \} = \frac{K_2 [\text{CAT}] [S]_T [\text{Os(VIII)}] \{ k_1 [\text{OH}^-] + k_2 K_1 \}}{1 + K_2 \text{Os(VIII)} [\text{OH}^-]}$$

OsO $_4$ exists in alkaline medium in the following two forms: [OsO $_4$ (H $_2$ O)(OH)] $^{-}$ and [OsO $_4$ (OH) $_2$] $^{2-}$.

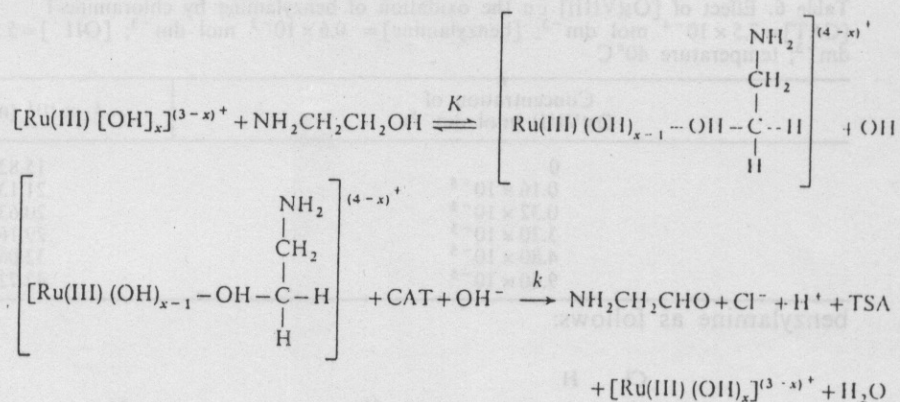
The sequence of reactions for ethanolamine is as follows:



Catalysis with Ru(III). The relevant rate data is given in Table 3. Reactions are first order in CAT, first order in ethanolamine, fractional order in Ru(III) and inverse fractional order in alkali. The mechanistic pathway and rate law are similar to the mechanism postulated with Os(VIII) and the corresponding rate law is:

$$\text{rate} = \frac{K_2 [\text{CAT}] [S]_T \text{Ru(III)} \{ k_1 [\text{OH}^-] + k_2 K_1 \}}{1 + K_2 \text{Ru(III)} [\text{OH}^-]}$$

The process may be depicted as follows. The active species of Ru(III) may be $[\text{Ru}(\text{H}_2\text{O})_{6-x}(\text{OH})_x]^{(3-x)+}$ in alkali medium.



Absence of catalysis by Os(VIII) and Ru(III) with ethylamine and benzylamine. Ru(III) does not catalyze the oxidation of benzylamine and ethylamine. The rates in the absence and in the presence of Ru(III) in both ethylamine and benzylamine are given in Tables 4 and 5.

Table 4. Effect of $[\text{Ru(III)}]$ on the oxidation of ethylamine by chloramine-T
 $[\text{CAT}] = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{ethylamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{OH}^-] = 22.0 \times 10^{-2} \text{ mol dm}^{-3}$; temperature 40°C

Concentration of Ru(III) (mol dm ⁻³)	$k_1 \times 10^4$ (min ⁻¹)
0	60.10
7.6×10^{-5}	61.23
19.0×10^{-5}	76.03

Table 5. Effect of $[\text{Ru(III)}]$ on the oxidation of benzylamine by chloramine-T
 $[\text{CAT}] = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{benzylamine}] = 0.6 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{OH}^-] = 5.5 \times 10^{-2} \text{ mol dm}^{-3}$; temperature 40°C

Concentration of Ru(III) (mol dm ⁻³)	$k_1 \times 10^4$ (min ⁻¹)
0	15.82
3.8×10^{-5}	17.36
7.6×10^{-5}	16.59

In the case of benzylamine oxidation with CAT it is observed that for an increase of sixty times of the catalyst Os(VIII), the increase in the reaction rate is twice (Table 6). This indicates that the increase in the rate may be treated as general salt effect and there is no catalysis. This gives the additional evidence that Ru(III) and Os(VIII) are specific catalysts when hydroxyl group is present in the molecule. As observed ethylamine and benzylamine which have only amino group are not catalyzed whereas ethanalamine having hydroxyl group in addition to amino group is specifically catalyzed by Ru(III) and Os(VIII).

The nature of the complex in uncatalyzed oxidation can not be quantified as they are electrostatic complexes formed between RNHCl and C-H bond of the organic compound. But the reaction pathway may be depicted in the case of ethylamine and

