

Kinetic Studies of Oxidation of Secondary Amines by Chloramine-T in Aqueous Perchloric Acid Medium Catalyzed by Ru(III)

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The kinetics of ruthenium(III) catalyzed oxidation of the secondary amines—diethylamine, dipropylamine, di-isopropylamine and dibutylamine by chloramine-T (CAT) in aqueous perchloric acid medium has been studied. The reaction rate shows a first order dependence each on CAT, *sec.*-amine and Ru(III). The reaction rate shows an inverse fractional order dependence on acid concentration. Added halide ions and the reaction product, *p*-toluenesulphonamide have no effect on the reaction rate. Variation of ionic strength and dielectric constant of the medium has no influence on the reaction. The activation parameters have been evaluated. It was observed that the rate of oxidation of *sec.*-amine by CAT increases in the order DEA < DPA < DBA < DiPA. Also it was found that ΔH^\ddagger and ΔS^\ddagger are linearly related and an isokinetic relationship is observed with isokinetic temperature β as 394 K, indicating enthalpy as controlling factor. Mechanisms consistent with experimental rate law have been proposed.

Key Words: Oxidation, Secondary amines, Chloramine-T, Ru(III) Catalyst, Kinetics.

INTRODUCTION

Oxidation of aliphatic amines by various oxidizing agents like N-bromosuccinamide, bromamine, cerium(IV), aqueous chlorine, bromamine-T and Mn(III)¹⁻⁵ have been reported. Aromatic N-haloamines are well known as mild oxidants and analytical reagents. Chloramine-T (CAT) is an important member of this group of oxidants. The kinetic and mechanistic aspects of this oxidant (CAT) has been well documented in literature^{6,7}. The present investigation reports the kinetic and mechanistic studies of oxidation of secondary amines by chloramine-T (CAT) in aqueous perchloric acid medium catalyzed by Ru(III).

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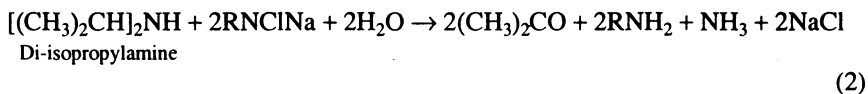
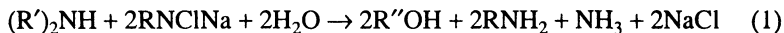
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EXPERIMENTAL

The oxidant chloramine-T (Lobo) sample was purified by Morris *et al.*⁸ method. An aqueous solution of CAT was prepared, standardized by the iodometric method and preserved in amber coloured bottles. The secondary amines: diethylamine (DEA), dipropylamine (DPA), di-isopropylamine (DIPA) and dibutylamine (DBA) procured from SD Fine Ltd. were employed after purification by distillation. Dibutylamine and ruthenium chloride solutions were prepared in 0.5 mol dm⁻³ of perchloric acid solution. The overall concentration of perchloric acid in the final stock solution of DBA was adjusted to 0.05 mol dm⁻³ by adding sodium hydroxide solution and allowance was made for the amount of HClO₄ present in the solution while preparing solution for kinetic runs. Ionic strength of the reaction mixture was kept at a high value using a concentrated solution of NaClO₄.

Kinetic Measurement: The reactions were carried out under pseudo-first order conditions by keeping an excess of secondary amine over CAT. The temperature was maintained within ± 0.1 K. The kinetics was followed by estimating the unreacted oxidant iodometrically. The rate constant (k') was evaluated from the plots of $\log [\text{CAT}]$ vs. time and was reproducible within $\pm 3\%$. Regression analysis of the experimental data was carried out on Casio Fx100s (VPAM) scientific calculator.

Stoichiometry and product analysis: Reaction mixture containing various ratios of [CAT] to [*sec.*-amine] in presence of aqueous perchloric acid 0.05 mol dm³ and Ru(III) were equilibrated as 323 K for 24 h. The unreacted oxidant was determined by iodometric titration. The obtained 1 : 2 stoichiometry is represented by eqns. (1) and (2).



where R = *p*-CH₃-C₆H₄SO₂; R' = ethyl for DEA, propyl for DPA and butyl for DBA, R'' = methyl or ethyl or propyl group.

The reaction product *p*-toluene sulphonamide (PTS) was detected by TLC using benzyl alcohol saturated with water as solvent and 0.5% vanillin in 1% HCl in ethanol as developing reagent ($R_f = 0.95$). The presence of aldehyde (ketone in the case of DIPA as substrate) in the reaction mixture was detected by preparing their 2,4-DNP derivatives and by Tollen's reagent test, further confirmed by HPLC⁸ and estimation of ammonia by slightly modified micro-Kjeldahl procedure.

RESULTS AND DISCUSSION

The kinetics of oxidation of secondary amines, *viz.*, diethylamine (DEA), dipropylamine (DPA), di-isopropylamine (DIPA) and dibutylamine (DBA) by CAT in aqueous perchloric acid catalyzed by Ru(III) at 323 K has been investigated.

The reactions were carried out in the presence of Ru(III) under pseudo-first order condition of $[sec.-amine] \gg [CAT]$. Plots of $\log [CAT]$ vs. time were linear ($r > 0.996$; plot not shown) indicating first order dependence of the reaction rate on $[CAT]$. Under identical conditions increase in $[sec.-amine]$ increases the rate constant (k'). Plot of $\log k'$ vs. $\log [sec.-amine]$ were linear ($r > 0.998$) with unit slope showing first order dependence of the rate on $[sec.-amine]$ (Table-1.) At constant $[Ru(III)]$, $[CAT]$, $[sec.-amine]$ and temperature, the reaction was studied with varying concentration of $HClO_4$. The plots $\log k'$ vs. $\log [HClO_4]$ were linear with negative slope (< 1) indicating inverse fractional order dependence of the rate on $[HClO_4]$ (Table-2). The rate increases with increase in $[Ru(III)]$ and plot of $\log k'$ vs. $\log [Ru(III)]$ were linear with unit slope indicating first order dependence of the rate on $[Ru(III)]$ (Table-2). Addition of chloride ion in the form of NaCl ($0.1-0.4 \text{ mol dm}^{-3}$), the reaction product PTS (1.0×10^{-3} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$) had no influence on the rate.

TABLE-1.
EFFECT OF VARYING REACTANT CONCENTRATIONS ON THE RATE

$[HClO_4] = 0.05 \text{ mol dm}^{-3}$, $[Ru(III)] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.5 \text{ mol dm}^{-3}$
Temperature = 312 K

$[CAT] \times 10^3$ (mol dm^{-3})	$[sec.-amine] \times 10^2$ (mol dm^{-3})	$k' \times 10^4 \text{ (s}^{-1}\text{)}$			
		DEA	DPA	DIPA	DBA
1.00	20.00	3.44	4.29	6.99	5.59
2.00	20.00	3.64	4.31	7.63	5.43
3.00	20.00	3.34	4.20	7.92	5.57
5.00	20.00	3.28	4.28	7.93	5.56
7.00	20.00	3.27	4.26	7.93	5.60
9.00	20.00	3.22	4.19	7.93	5.55
5.00	05.00	0.82	1.05	1.99	1.40
5.00	10.00	1.65	2.11	4.00	2.79
5.00	15.00	2.47	3.56	6.03	4.17
5.00	20.00	3.28	4.28	7.93	5.56
5.00	25.00	—	5.03	—	6.74
5.00	30.00	4.93	6.29	11.77	8.34
5.00	40.00	6.58	8.31	15.96	10.08

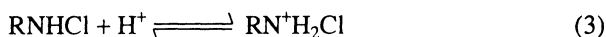
TABLE-2
EFFECT OF VARYING PERCHLORIC ACID AND Ru(III)
CONCENTRATIONS ON THE RATE

[CAT = 5.0×10^{-3} mol dm⁻³, [sec.-amine] = 0.02 mol dm⁻³, μ = 0.5 mol dm⁻³
Temperature = 312 K

[HClO ₄] × 10 ³ (mol dm ⁻³)	[Ru(III)] × 10 ⁵ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)			
		DEA	DPA	DIPA	DBA
5.00	2.50	3.28	4.28	7.93	5.56
7.50	2.50	2.71	3.53	6.70	4.56
10.00	2.50	2.34	3.01	5.88	3.91
15.00	2.50	1.91	2.53	4.95	3.28
20.00	2.50	1.66	2.10	4.37	2.85
25.00	2.50	1.48	1.81	3.97	2.43
5.00	1.00	1.32	1.70	3.71	2.23
5.00	2.50	3.28	4.28	7.93	5.56
5.00	5.00	6.54	8.36	15.97	11.10
5.00	7.50	9.81	13.62	23.60	16.59
5.00	10.00	13.05	15.27	—	22.21

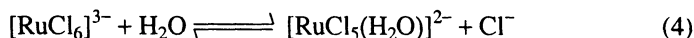
Variation of the ionic strength of the medium by adding sodium perchlorate (0.1–0.4 mol dm⁻³) has negligible effect and variation of dielectric constant of the medium by adding methanol (0–30% v/v) has negligible effect on the reaction rate. The reaction was studied at various temperatures in the range of 318 K and 333 K. The activation parameters, namely energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger), were obtained from Arrhenius plot of $\log k'$ vs. $1/T$, which were linear. The kinetics and activation parameters data obtained are presented in Table-3. Addition of reaction mixture to aqueous acrylamide monomer did not initiate polymerization indicating the absence of formation of free radical species in the reaction sequence.

Chloramine-T has been thoroughly investigated by Bishop and Jennings¹⁰ and Higuchi¹¹. The possible reactive oxidizing species in acidified chloramine solution are RNHCl, RNCl₂, HOCl and H₂OCl⁺. The involvement of RNCl₂ in the mechanism is expected to lead to second order rate law and if HOCl was to be primarily involved, a first order retardation by addition of PTS is expected. Both the former and latter were contrary to experimental observation. Narayanan¹² and Subashini¹³ *et al.* have reported that CAT protonates at pH 2 [eqn. (3)] and the value of second protonation constant is 102 at 25°C.

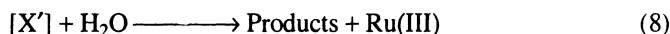
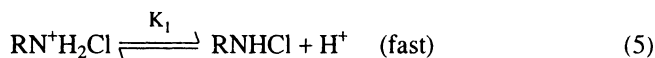


In the present study, the negative fractional order in $[\text{H}^+]$ indicates that the deprotonation of $\text{RN}^+\text{H}_2\text{Cl}$ results in the reformation of RNHCl, which can be considered to be the active oxidizing species involved in the mechanism of oxidation of the secondary amines.

In the acid solution, the ruthenium trichloride exists as $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$, $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ and *cis*- and *trans*- $[\text{RuCl}_2(\text{H}_2\text{O})_2]^{3+}$. These species have been identified by their electronic spectra. The existence of RuCl_3 , RuCl^{2+} and RuCl_2^+ in dilute solution of HCl of RuCl_3 has been shown by Cady¹⁴, Connick and Fine¹⁵. $\text{Ru}(\text{III})$, however, can also exist in the following ligand substitution equilibrium in an acid medium



In the present case, negligible effect of chloride ion and ionic strength indicates that $[\text{RuCl}_3]^{3-}$ is the most likely catalyzing species which interacts with the substrate to form a complex intermediate. UV spectral study reveals that the complex formation takes place only between $\text{Ru}(\text{III})$ and the substrate. Thus in the proposed mechanism (**Scheme-1**) the $[\text{Ru}(\text{III})\text{-substrate}]$ complex $[\text{X}]$ reacts with RNHCl in the slow step (rate determining step) to form the intermediate X' which is disproportionate to the products.



Scheme-1

where S represents *sec.*-amine, $[\text{X}]$ and $[\text{X}']$ represent complex intermediate species. **Scheme-1** leads to the rate law

$$\text{Rate} = \frac{k_3 K_1 K_2 [\text{CAT}][\text{S}][\text{Ru}(\text{III})]}{[\text{H}^+] + K_1} \quad (9)$$

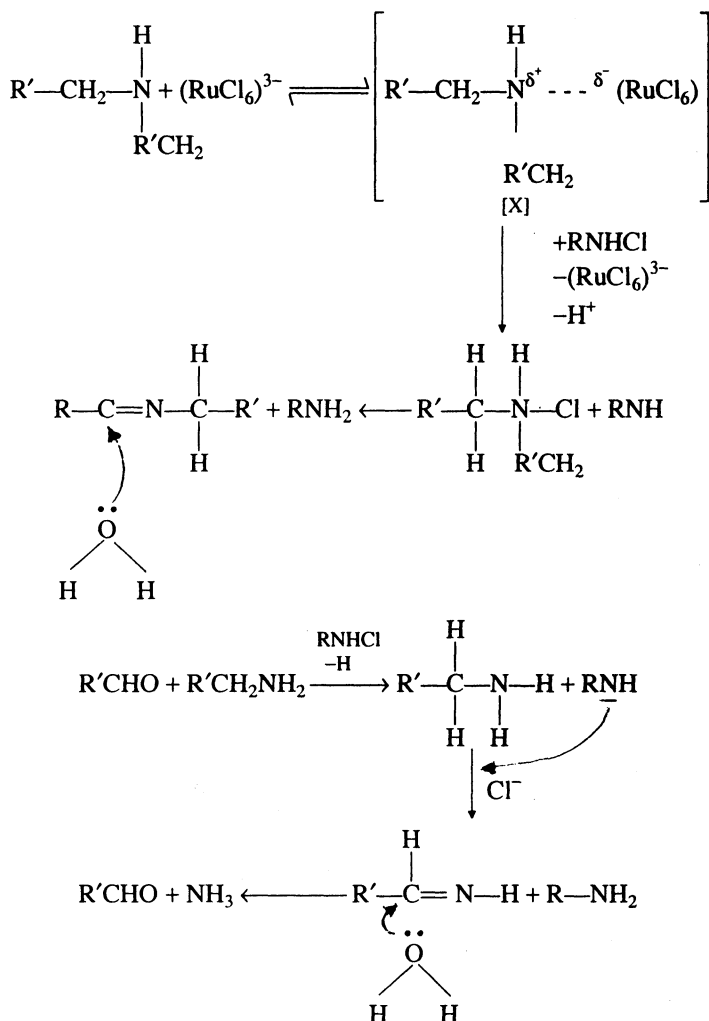
which is in agreement with experimental results which includes first order dependence on $[\text{CAT}]$, [*sec.*-amine], $[\text{Ru}(\text{III})]$ and inverse fractional order dependence on $[\text{HClO}_4]$.

Since $\text{rate} = k'[\text{CAT}]$, equation (8) can be transformed into the following equation:

$$\frac{1}{k'} = \frac{[\text{H}^+]}{k_3 K_2 K_1 [\text{S}][\text{Ru}(\text{III})]} + \frac{1}{k_2 k_3 [\text{S}][\text{Ru}(\text{III})]} \quad (10)$$

The plot of $1/k'$ vs. $[\text{H}^+]$ at constant $[\text{S}]$ and $[\text{Ru}(\text{III})]$ is found to be linear ($r > 0.997$) (plot not shown). From the intercept and slope of the plot, K_1 and the product $K_2 k_3$ were determined (data not given). The protonation equilibrium constant $1/K_1$ calculated indicated that the rate of protonation is large and therefore, the concentration of RNHCl is small, which is reflected in slow rate of reaction. This is supported by the experimentally observed data.

It is observed that the rate of oxidation of *sec.*-amine by CAT increases in the order DEA < DPA < DBA < DIPA. The relative magnitudes of energies of activation for the *sec.*-amine (Table-3) indicate that the reactions are enthalpy controlled. This is verified by calculating the isokinetic temperature β as 394 K, from the slope of plot of ΔH^\ddagger vs. ΔS^\ddagger ($r > 0.998$) (plot not shown) which is higher than that of experimental temperature. Further confirmation of isokinetic relationship was done by Exner criterion¹⁶ by plotting $\log k_{333}$ vs. $\log k_{318}$, which is linear ($r > 0.999$; plot not shown). From Exner slope, calculated value of β was found to be 392 K. The fairly large negative value of entropy of activation indicates the formation of rigid transition state. A suitable path of mechanism is given by **Scheme-2**.



$\text{R}' = \text{CH}_3$ and CH_3CH_2 for diethylamine and dipropylamine respectively

$\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$ for CAT

Scheme-2. Mechanism of oxidation of *sec.*-amine by CAT in aq. perchloric acid medium catalyzed by Ru(III)

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE OXIDATION
SECONDARY AMINES BY CAT IN PERCHLORIC ACID
CATALYZED BY Ru(III).

Thermodynamic parameters	DEA	DPA	DIPA	DBA
E_a (kJ mol ⁻¹)	65.88	62.94	52.86	58.17
ΔH^\ddagger (kJ mol ⁻¹)	63.17	60.23	50.15	55.46
ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	-116.80	-123.64	-149.72	-136.20
ΔG^\ddagger (kJ mol ⁻¹)	7.16	6.81	5.45	6.15

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(Received: 2 August 2004; Accepted: 19 January 2005)

AJC-4062