Review

Ru(III)-catalysed oxidation of some amines by chloramine-T in hydrochloric acid medium: Mechanistic aspects and kinetic modeling

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Abstract

The kinetics of oxidation of five amines viz., ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), aminoethylpiperazine (AEP) and isophoronediamine (IPDA) by sodium N-chloro-p-toluenesulfonamide or chloramine-T (CAT) in the presence of HCl and Ru(III) chloride was studied at 303 K. The five reactions followed identical kinetics and the experimental rate law is rate $= k[CAT]_0[amine]_0^x[H^+]^y[Ru(III)]^z$, where x, y and z are fractions. A variation of the ionic strength or dielectric constant of the medium and the addition of halide ions and p-toluenesulfonamide had no significant effect on the rate of the reaction. The solvent isotope effect has been studied in D_2O medium. The activation parameters have been evaluated from the Arrhenius plots. Under comparable experimental conditions, the rate of oxidation of amines increases in the order: AEP > TETA > DETA > EDA > IPDA. An isokinetic relationship is observed with $\beta = 377$ K, indicating enthalpy as a controlling factor. Oxidation products were identified. $CH_3C_6H_4SO_2\overset{+}{N}H_2Cl$ of the oxidant has been postulated as the reactive oxidizing species. Further, the kinetics of Ru(III)-catalysed oxidation of these amines have been compared with unanalyzed reactions (in the absence of Ru(III) catalyst) and found that the catalysed reactions are 2–3-fold faster. The catalytic constant (K_C) was also calculated for each amine at different temperatures from the plots of $\log K_C$ against $1/T$, values of activation parameters with respect to the catalyst have been evaluated. The observed results have also been explained by a plausible mechanism and the related rate law has been deduced.

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1. Introduction

Amines are nitrogen containing bases that find wide applications in industry as additives in plating complexes baths, as reagents in the synthesis of dyes and polymeric materials, and as potential ligands for metal complexes used in heterogeneous catalysis in addition to as curing agents for epoxy resins to improve the properties of cured systems [1,2]. They also play an important role in biological systems. Oxidation of amines is of importance, as it adds to the body of knowledge of redox chemistry. The oxidation products depend on the type of oxidant, on the reaction medium and on the nature of the alkyl groups present. Because of these, amines have been oxidized by a number of oxidizing agents under various experimental conditions [3,4]. The amines selected to our oxidation kinetic study are ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), aminoethylpiperazine (1-(2-aminoethyl) piperazine; AEP) and isophoronediamine (5-amino-1,3,3-trimethylcyclohexanemethylamine; IPDA) as they are used as curing agents in epoxy resins. In order to understand the curing kinetics of various amines with epoxies, it is very essential to understand the oxidation kinetics of amines chosen in our studies by an oxidizing agent. An extensive literature survey reveals meager information on the oxidation of selected amines viewed from their kinetic and mechanistic aspects. Hence, we felt it would be worthwhile to investigate the oxidative behavior of positive halogen compounds with amines substrates to explore the kinetics and mechanistic aspects of the redox reactions. Hence, the present kinetic study gives an impetus as the substrate amines are used as curing agents in epoxy resins.

Chloramine-T (CAT; sodium *N*-chloro-*p*-toluenesulfonamide) is the most important member of organic haloamine family and behaves as an oxidizing agent in both acidic and alkaline media. Mechanistic aspects of many of its reaction have been well documented [5–10]. However, literature survey revealed that, there are sparse efforts made from the kinetic and mechanistic view points on the oxidation of chosen amines by CAT.

Ruthenium(III) chloride (Ru(III)) is the important platinum group metal ion and has been widely used as a homogeneous catalyst in various redox reactions [11]. The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radicals and different oxidizing states of Ru(III). Although many complexes of Ru(III) with various organic and inorganic substances have been reported [11–16], a literature survey shows a very few kinetic investigations on the oxidation reactions of amines involving Ru(III)

as a homogeneous catalyst. Preliminary experimental results revealed that the reactions of selected amines with CAT in HCl medium without a catalyst were 2–3-fold sluggish, but the reactions become facile in the presence of a micro quantity of Ru(III) catalyst. Therefore, in order to explore the mechanism of amine–CAT reactions in acid medium and also to study the catalytic action of Ru(III) in this reaction, Ru(III) as a catalyst is selected in the present work. Based on the above facts, in the present communication, we report the results of the detailed investigation on the kinetic and mechanistic aspects of Ru(III)-catalysed oxidation of amines by CAT in HCl medium at 303 K. Objectives of the present study are to: (i) elucidate a plausible mechanism, (ii) deduce an appropriate rate law, (iii) identify the oxidation products, (iv) ascertain the various reactive species, (v) assess the relative rates of oxidation of amines towards CAT, (vi) establish the isokinetic relationships using thermodynamic parameters, (vii) find the catalytic efficiency of Ru(III) and (viii) compare the reactivity of CAT towards amines with that under uncatalysed oxidation.

2. Results and discussion

The kinetics of oxidation of five amines viz., ethylenediamine, diethylenetriamine, triethylenetetramine, aminoethylpiperazine and isophoronediamine by CAT have been investigated at several initial concentrations of the reactants in the presence of HCl and Ru(III) chloride catalyst at 303 K.

2.1. Effect of varying reactant concentrations on the rate

The reaction carried out in the presence of Ru(III) catalyst and HCl, under pseudo first-order conditions of $[amine]_0 \gg [CAT]_0$ gave linear plots of $\log[CAT]$ versus time ($r > 0.9910$). The linearity of these plots, together with the constancy of the slopes obtained at various $[CAT]_0$, indicate a first-order dependence of the reaction rate on $[CAT]_0$. The pseudo first-order rate constants (k') obtained are listed in Table 1. Under the similar experimental conditions, an increase in $[amine]_0$ increased the k' values (Table 1). Plots of $\log k'$ versus $\log[amine]_0$ were linear ($r > 0.9859$) with fractional slopes (0.3–0.5), showing a fractional-order dependence of rate on $[amine]_0$. Further, plots of k' versus $[amine]_0$ were linear ($r > 0.9892$) having an *Y*-intercept, confirming the fractional-order dependence on $[amine]_0$.

Table 1
Effect of varying reactant concentrations on the reaction rate at 303 K

$10^3[CAT]_0$ (mol dm^{-3})	$10^2[amine]_0$ (mol dm^{-3})	$10^4 k'$ (s^{-1})				
		EDA	DETA	TETA	AEP	PDA
0.50	2.00	1.55	3.19	3.20	6.00	1.50
1.00	2.00	1.55	3.20	3.20	6.00	1.50
1.50	2.00	1.56	3.20	3.21	6.10	1.50
2.00	2.00	1.56	3.15	3.22	6.10	1.51
4.00	2.00	1.56	3.15	3.22	6.10	1.51
1.00	0.50	1.00	1.84	2.40	3.70	1.50
1.00	1.00	1.19	2.60	3.00	4.60	1.10
1.00	2.00	1.50	3.77	3.60	6.00	1.50
1.00	4.00	1.83	4.74	4.50	7.50	2.00
1.00	6.00	2.00	6.40	5.00	11.13	2.60

[HCl] = 1.0×10^{-2} mol dm^{-3}; Ru(III) = 1.0×10^{-4} mol dm^{-3}.

2.2. Effect of varying HCl and Ru(III) concentrations on the rate

The rate increased with increase in [HCl] (Table 2) and plots of $\log k'$ versus $\log$[HCl] were linear ($r > 0.9933$) with fractional slopes (0.2–0.3), showing a fractional-order dependence of the rate on [HCl]. The reaction rate increased with increase in [Ru(III)] (Table 2). Plots of $\log k'$ versus $\log$[Ru(III)] were linear ($r > 0.9881$) with fractional slopes (0.2–0.5), confirming fractional-order dependence on [Ru(III)].

2.3. Effect of varying H$^+$ ion and Cl$^-$ ion concentrations on the rate

At constant [H$^+$] = 0.01 mol dm^{-3} maintained with HCl, the addition of NaCl (1.0×10^{-2} to 8.0×10^{-2} mol dm^{-3}) did not affect the rate of the reaction. Hence, the dependence of rate on [HCl] confirms the effect of [H$^+$] only.

2.4. Effect of varying concentration of p-toluenesulfonamide (PTS) on the rate

Addition of PTS (0.5×10^{-2} to 4.0×10^{-2} mol dm^{-3}) to the reaction mixture did not effect the rate significantly. This

indicates that PTS is not involved in any step prior to the rate determining step (r.d.s.) in the scheme proposed.

2.5. Effect of varying ionic strength and dielectric constant of the medium on the rate

The effect of ionic strength of the medium on the rate was carried from 0.1 to 0.5 mol dm^{-3} using NaClO$_4$ solution with other constant experimental conditions. The ionic strength showed negligible effect on the reaction rate indicating involvement of a non-ionic species in the rate determining step. Subsequently the ionic strength of the reaction mixture was not kept constant for kinetic runs. The dielectric constant of the solvent medium was varied by adding methanol (0–30%, v/v), which did not had any pronounced influence on the rate.

2.6. Effect of varying temperature on the rate

The reaction was studied at different temperatures (298–318 K), keeping other experimental conditions constant. From the linear Arrhenius plots of $\log k'$ versus $1/T$ (Fig. 1; $r > 0.9815$), values of activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) for the composite reaction were evaluated. These data are summarized in Table 3.

Table 2
Effect of varying HCl and Ru(III) concentrations on the reaction rate at 303 K

$10^2[HCl]$ (mol dm^{-3})	$10^4[RuCl_3]$ (mol dm^{-3})	$10^4 k'$ (s^{-1})				
		EDA	DETA	TETA	AEP	IPDA
0.50	1.00	1.30	3.20	3.20	3.70	0.07
1.00	1.00	1.50	4.10	3.60	4.30	1.50
2.00	1.00	1.78	5.03	4.20	5.20	1.70
4.00	1.00	2.04	6.03	4.60	6.09	1.90
6.00	1.00	2.22	7.20	5.20	7.00	2.05
1.00	0.10	1.01	3.00	2.60	3.40	0.09
1.00	0.50	1.12	3.40	3.12	4.20	1.10
1.00	1.00	1.50	4.00	3.60	5.50	1.50
1.00	1.50	1.70	4.60	4.60	6.20	1.60
1.00	2.00	1.90	5.20	5.20	7.00	2.00

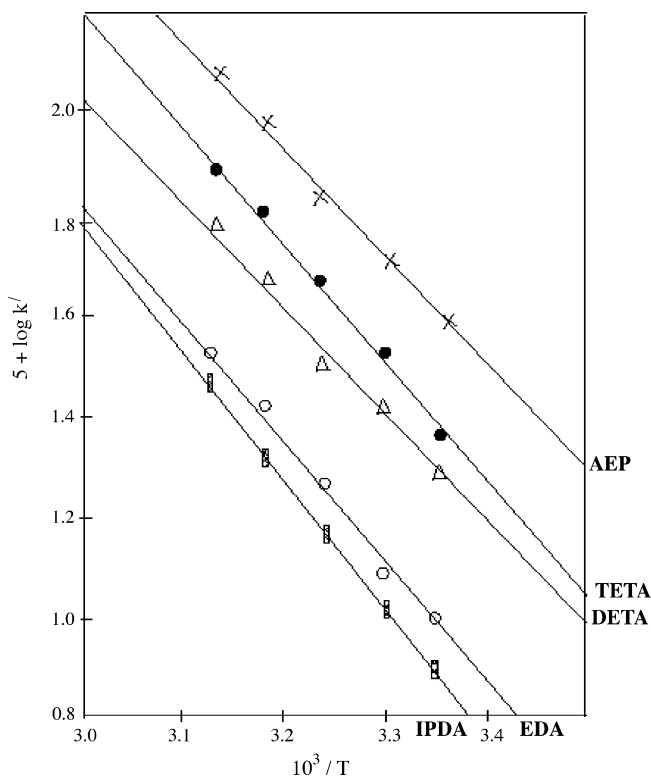[CAT]$_0$ = 1.00×10^{-3}; [amine]$_0$ = 2.00×10^{-2}.

Fig. 1. Plot of $\log k'$ vs. $1/T$. Experimental conditions are as in Table 3.

2.7. Effect of solvent isotope on the rate

Studies of the reaction rate in D_2O medium for ethylenediamine as a probe revealed that while $k'(H_2O) = 1.10 \times 10^{-4}$ and $k'(D_2O) = 1.30 \times 10^{-4}$. The solvent isotope effect $k'(H_2O)/k'(D_2O) = 0.85$ for ethylenediamine.

2.8. Test for free radicals

The addition of the reaction mixture to an aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of formation of free radical species in situ in the reaction sequence. The controlled experiments were also performed under the same reaction conditions but without CAT.

2.9. Reaction mechanism and rate law

In general, CAT undergoes a two-electron change in its reactions. The reduction potential of CAT/PTS is pH dependent [10] and decreases with an increase in pH of the medium, having values of 1.14 V at pH 0.65 and 0.50 V at pH 12. Chloramine-T behaves like a strong electrolyte in aqueous solutions and depending on the pH of the medium, CAT furnishes different equilibria in solutions [17–20].

The possible oxidizing species in acidified CAT solutions are the conjugate acid TsNHCl, the dichloramine-T TsNCl$_2$, the hypochlorous acid HOCl, and perhaps H$_2$OCl. TsNCl$_2$ species has been ruled out as the oxidizing species based on the fact that, the rate is not retarded by the added TsNH$_2$, and also the rate law should predict a second-order dependence of the rate on [CAT]$_0$.

Table 3
Temperature dependence on the reaction rate and values of composite activation parameters for the oxidation of amines by CAT in presence and absence of Ru(III) catalyst

Temperature (K)	EDA	DETA	TETA	AEP	IPDA
	$10^4 k'$ (s^{-1})				
298	0.90 (0.17)	2.40 (0.65)	1.90 (0.68)	4.00 (1.50)	0.8 (0.16)
303	1.10 (0.30)	3.09 (0.80)	2.80 (1.12)	5.00 (2.00)	1.00 (0.30)
308	1.50 (0.45)	3.76 (1.02)	3.61 (1.34)	6.00 (2.80)	1.50 (0.42)
313	2.30 (0.56)	5.70 (1.11)	4.68 (1.74)	8.50 (3.90)	2.20 (0.54)
318	3.10 (0.91)	9.10 (1.31)	5.80 (2.95)	12.6 (5.11)	3.00 (0.90)
E_a (kJ mol^{-1})	50.6 (74.0)	44.16 (68.2)	39.59 (64.6)	34.74 (59.4)	52.9 (76.2)
$\Delta H^{\#}$ (kJ mol^{-1})	51.4 ± 0.38 (71.5 ± 0.38)	41.4 ± 0.30 (65.6 ± 0.40)	37.1 ± 0.40 (62.3 ± 0.19)	32.2 ± 0.56 (57.2 ± 0.90)	50.4 ± 0.67 (73.5 ± 0.41)
$\Delta G^{\#}$ (kJ mol^{-1})	83.2 ± 0.13 (86.7 ± 0.28)	80.7 ± 0.17 (84.2 ± 0.67)	81.2 ± 0.57 (83.3 ± 0.90)	79.2 ± 0.55 (82.1 ± 0.60)	83.3 ± 0.09 (86.7 ± 0.38)
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−103 ± 0.36 (−49.3 ± 0.54)	−127 ± 0.45 (−60.4 ± 0.76)	−143 ± 0.31 (−69.7 ± 0.52)	−154 ± 0.50 (80.9 ± 0.70)	−107 ± 0.3 (−42.4 ± 0.32)
Log A	9.36 ± 0.16 (12.2 ± 0.11)	8.09 ± 0.21 (11.5 ± 0.40)	7.26 ± 0.16 (11.1 ± 0.24)	6.72 ± 0.19 (10.5 ± 0.20)	9.16 ± 0.14 (12.5 ± 0.22)

[CAT]$_0$ = 1.0 × 10^{-3}; [amine]$_0$ = 2.0 × 10^{-2}; [HCl] = 1.0 × 10^{-2} mol dm^{-3}; Ru(III) = 1.0 × 10^{-4} mol dm^{-3}. Values in parentheses refer to the reaction in absence of Ru(III) catalyst. Experimental condition is same as above without Ru(III) catalyst.

Both are contrary to experimental observations. If HOCl were to be involved as an active oxidant species, a first-order retardation of rate by the added $TsNH_2$ would expect. Since no such effect was noticed, the species HOCl was also ruled out. Based on the knowledge of equilibrium, disproportionations, and hydrolysis constant of reactions, Bishop and Jennings [18] as a first approximation, have calculated the concentrations of different species in $0.05\,mol\,dm^{-3}$ CAT solution at different pH. Therefore, the conjugate acid, TsNHCl, is the predominant species under acidic conditions. Furthermore, variation of ionic strength of the medium or addition of reduction product of CAT, $TsNH_2$, has virtually no effect on the rate. The dependence of rate on $[H^+]$ indicates protonation of the oxidant. Further, the formation of the diprotonated species with a protonation constant of $1.02 \times 10^2\,mol\,dm^{-3}$ at $25\,^\circ C$ has been reported (Eq. (1)) for CAT acid solutions [21,22]:

$$TsNHCl + H^+ \rightleftharpoons Ts\overset{+}{N}H_2Cl \qquad (1)$$
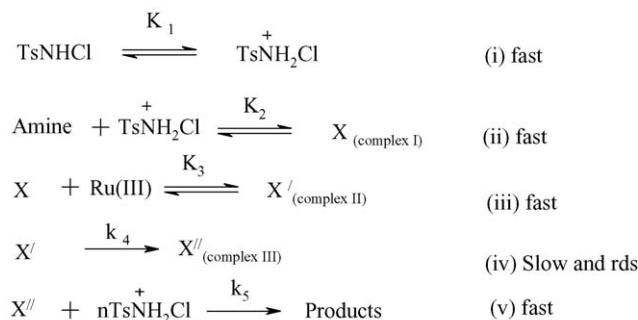
In the present investigations, the acceleration of rate by $[H^+]$ ion indicates that the protonated oxidant ($Ts\overset{+}{N}H_2Cl$) is the active oxidizing species.

Electronic spectral studies by Cady and Connick [23] and Connick and Fine [24] reveal that species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$ do not exist in aqueous solutions of $RuCl_3$. A study on the oxidation states of ruthenium has shown that Ru(III) exists [25–27] in the acid medium as

$$RuCl_3 \cdot xH_2O + 3HCl \rightarrow [RuCl_6]^{3-} + xH_2O + 3H^+ \qquad (2)$$

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{2-} + Cl^+ \qquad (3)$$

Scheme 1. A general scheme for the Ru(III)-catalysed oxidation of amines by CAT in HCl medium.

Singh et al. [28,29] employed the above equilibrium in Ru(III)-catalysed oxidations of primary alcohols by bromamine-T and of glycols by N-bromoacetamide in acid medium. However, in the present study addition of Cl^- ion in the form of NaCl at fixed $[H^+]$ had no effect on the rate, indicating that equilibrium (3) does not play any role in the reaction. Hence, the complex ion $[RuCl_5(H_2O)]^{2-}$ is assumed to be the reactive catalysing species. Similar results have been reported in the Ru(III)-catalysed oxidation of several other substrates by N-haloamines [30–32].

Based on the preceding discussion, a detailed mechanistic interpretation (Scheme 1) for the Ru(III)-catalysed amine–CAT reaction in acidic medium has been proposed to substantiate the observed experimental results.

Here, $n = 1$ for ethylenediamine, aminoethylpiperazine and isophoronediamine, 3 for diethylenetriamine and 7 for triethylenetetramine. In Scheme 1, X, X' and X'' represents the complex intermediate species whose structures are shown in Schemes 2–6, where a detailed mechanistic interpretation of

Scheme 2. Oxidation of ethylenediamine by CAT.
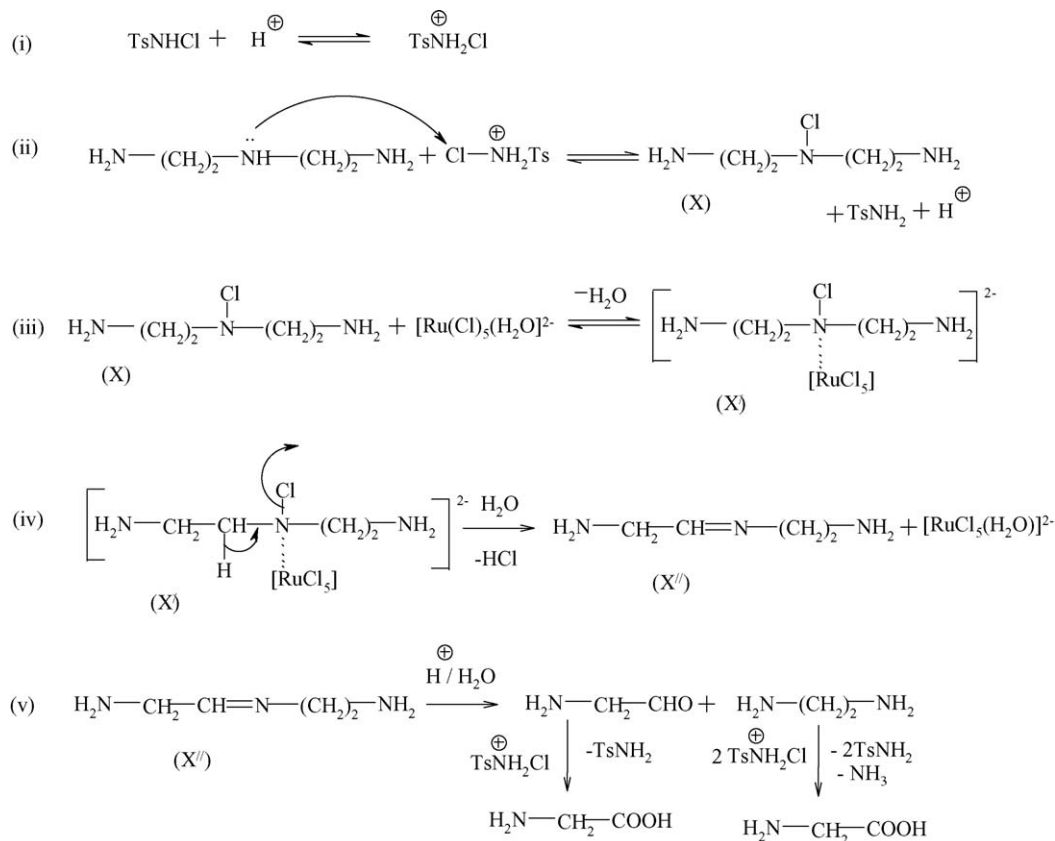
Scheme 3. Oxidation of diethylenetriamine by CAT.

Ru(III)-catalysed—each amine–CAT reaction in acid medium is depicted.

The total effective concentration of CAT is $[CAT]_t$, then

$$[CAT]_t = [TsNHCl] + [Ts\overset{+}{N}H_2Cl] + [X] + [X'] \qquad (4)$$

Solving for $[TsNHCl]$, $[Ts\overset{+}{N}H_2Cl]$ and $[X]$ in terms of $[X']$ from steps (i)–(iii) of Scheme 1, one gets

$$[TsNHCl] = \frac{[X']}{K_1 K_2 K_3 [amine][H^+][Ru(III)]} \qquad (5)$$

$$[Ts\overset{+}{N}H_2Cl] = \frac{[X']}{K_2 K_3 [amine][Ru(III)]} \qquad (6)$$

$$[X] = \frac{[X']}{K_3 [Ru(III)]} \qquad (7)$$

By substituting for $[TsNHCl]$, $[Ts\overset{+}{N}H_2Cl]$ and $[X]$ from Eqs. (5)–(7) in Eq. (4) and solving for $[X']$, one obtains

$$[X'] = \frac{K_1 K_2 K_3 [CAT]_t [amine][H^+][Ru(III)]}{1 + K_1[H^+] + K_1 K_2 [amine][H^+]} \\ {+ K_1 K_2 K_3 [amine][H^+][Ru(III)]} \qquad (8)$$

From the slow step (iv) of Scheme 1:

$$rate = k_4 [X'] \qquad (9)$$

Upon substituting for $[X']$ from Eq. (8) in Eq. (9), Eq. (9) yields the following rate law (10):

$$rate = \frac{K_1 K_2 K_3 k_4 [CAT]_t [amine][H^+][Ru(III)]}{1 + K_1[H^+] + K_1 K_2 [amine][H^+]} \\ {+ K_1 K_2 K_3 [amine][H^+][Ru(III)]} \qquad (10)$$

Rate law (10) is in good agreement with the observed kinetic data. The proposed scheme and the derived rate law are also substantiated by the experimental observations discussed below.
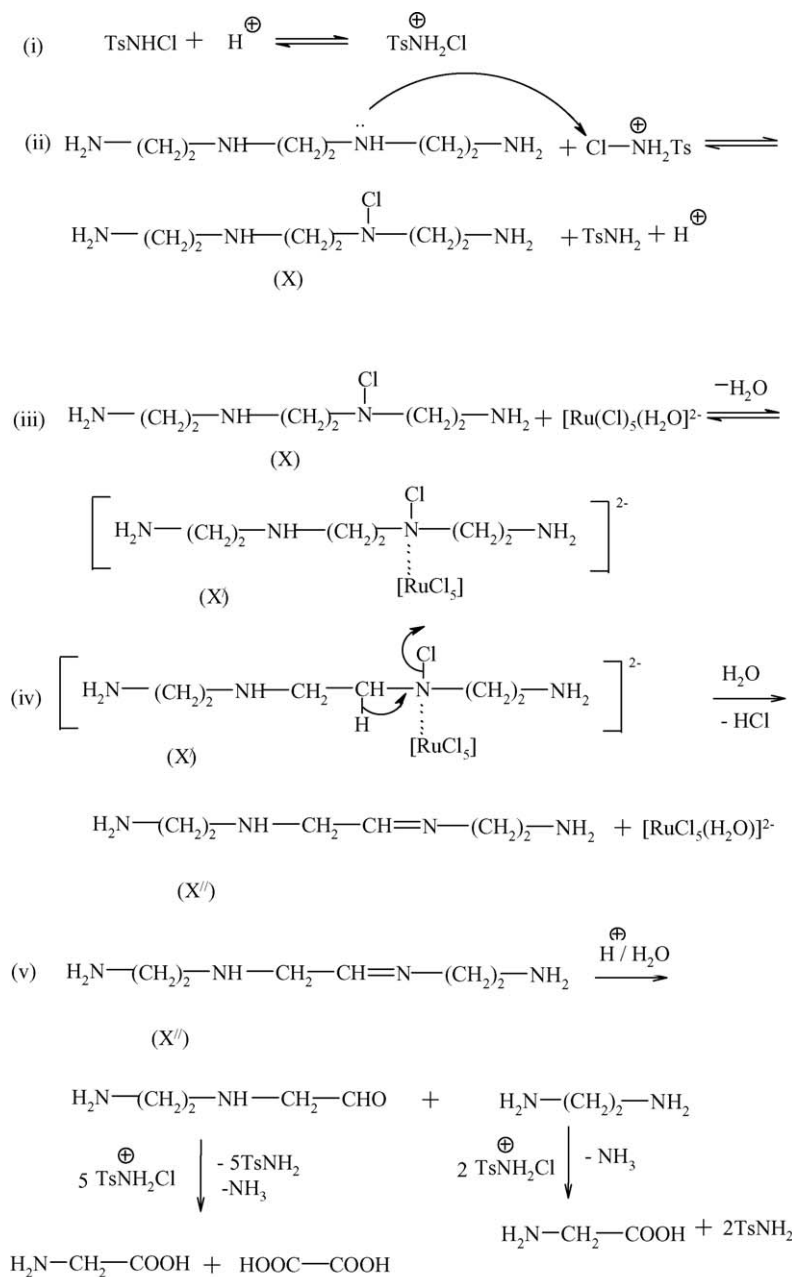
2.10. Effect of solvent isotope

The solvent isotope effect observed corroborates the proposed mechanism and the derived rate expression for a reaction involving a fast equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O since D_3O^+ and OD^- which are stronger acid and stronger base (~2–3 times greater), respectively, than H_3O^+ and OH^- ions [33,34]. The increase of reaction rate with D_2O observed in the present studies and the solvent isotope effect which is $k'(H_2O)/k'(D_2O) < 1$ conform the above theory. However, the small magnitude of the effect can be attributed to the fractional-order dependence on $[H^+]$.

2.11. Effect of solvent composition

The effect of varying solvent composition on the rate of reaction has been described in detail earlier in various monographs

(i) $TsNHCl + \overset{\oplus}{H} \rightleftharpoons \overset{\oplus}{TsNH_2Cl}$

(ii) $H_2N-(CH_2)_2-NH-(CH_2)_2-\overset{\cdot\cdot}{N}H-(CH_2)_2-NH_2 + Cl-\overset{\oplus}{N}H_2Ts \rightleftharpoons$

$H_2N-(CH_2)_2-NH-(CH_2)_2-\overset{\overset{Cl}{|}}{N}-(CH_2)_2-NH_2 + TsNH_2 + \overset{\oplus}{H}$

(X)

(iii) $H_2N-(CH_2)_2-NH-(CH_2)_2-\overset{\overset{Cl}{|}}{N}-(CH_2)_2-NH_2 + [Ru(Cl)_5(H_2O)]^{2-} \overset{-H_2O}{\rightleftharpoons}$

(X)

$\left[H_2N-(CH_2)_2-NH-(CH_2)_2-\overset{\overset{Cl}{|}}{N}-(CH_2)_2-NH_2 \right]^{2-}$

(X)   [RuCl₅]

(iv) $\left[H_2N-(CH_2)_2-NH-CH_2-\overset{\overset{|}{C}H}{\underset{H}{}}-\overset{\overset{Cl}{|}}{N}-(CH_2)_2-NH_2 \right]^{2-} \overset{H_2O}{\underset{-HCl}{\longrightarrow}}$

(X)   [RuCl₅]

$H_2N-(CH_2)_2-NH-CH_2-CH=N-(CH_2)_2-NH_2 + [RuCl_5(H_2O)]^{2-}$

(X″)

(v) $H_2N-(CH_2)_2-NH-CH_2-CH=N-(CH_2)_2-NH_2 \overset{\overset{\oplus}{H}/H_2O}{\longrightarrow}$

(X″)

$H_2N-(CH_2)_2-NH-CH_2-CHO + H_2N-(CH_2)_2-NH_2$

$5\ \overset{\oplus}{TsNH_2Cl} \Big| \begin{array}{l} -5TsNH_2 \\ -NH_3 \end{array}$ $2\ \overset{\oplus}{TsNH_2Cl} \Big| -NH_3$

$H_2N-CH_2-COOH + 2TsNH_2$

$H_2N-CH_2-COOH + HOOC-COOH$

Scheme 4. Oxidation of triethylenetetramine by CAT.

[35–38]. For the limiting case of zero angle of approach between two dipoles or an ion–dipole systems, Amis [38] has shown that a plot of $\log k'$ versus $1/D$ gives a straight line having a negative slope for the reaction involving a negative ion and dipole or between dipoles, while a positive slope was obtained for a positive ion–dipole interaction. The total absence of the effect of varying dielectric constant on the rate observed in present work cannot be explained by Amis theory [38]. Applying the Born equation [37] Laidler and co-workers [36] derived the following equation for a dipole–dipole reaction:

$$\ln k' = \ln k_0 + \frac{3}{8}kT\frac{2}{D-1}\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_\#^2}{r_\#^3} \right] \qquad (11)$$

where k_0 is the rate constant in medium of infinite dielectric constant, μ the dipole moment, and r refers to the radii of the reactants and activated complex. It is seen that the rate should be greater in a medium of lower dielectric constant, when $r_\#^3 > r_A^3 + r_B^3$. On the other hand, $r_\#^3 \approx r_A^3 + r_B^3$ implies the absence of dielectric constant effect on the rate, as observed in the present investigation, signifies that the transition state is not very different from the reactant.

2.12. Activation parameters in presence of Ru(III)

It is seen from Table 3 that the rate of oxidation of amines by CAT in presence of HCl and Ru(III) catalyst increased in
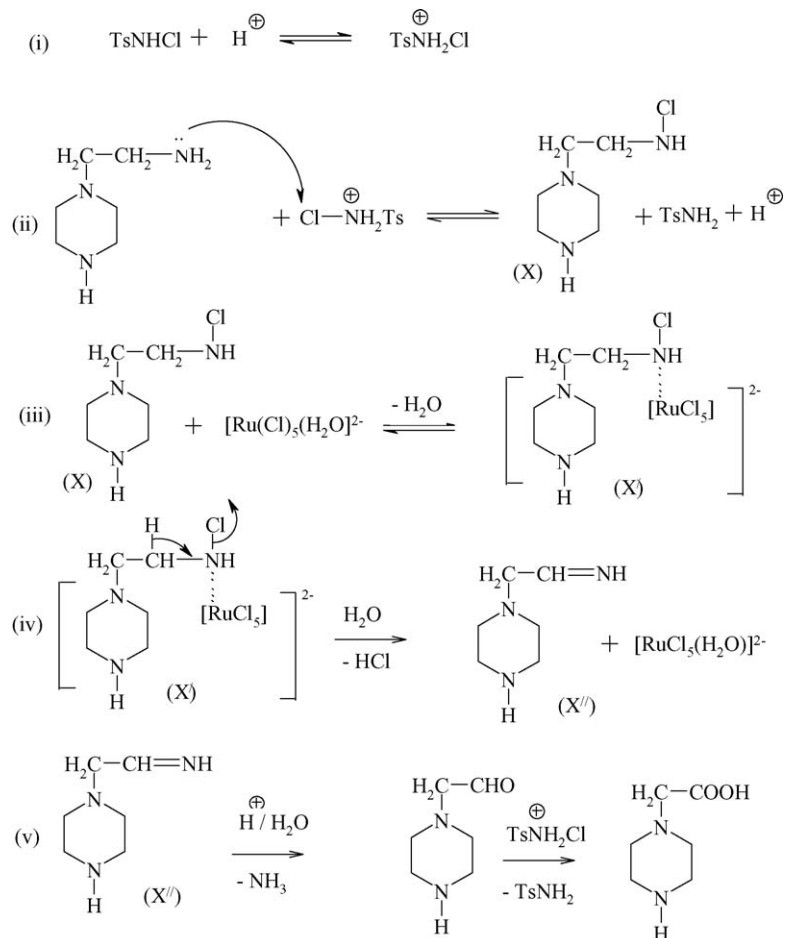
Scheme 5. Oxidation of aminoethylenepepirizine by CAT.

the order: AEP > TETA > DETA > EDA > IPDA. This reactivity trend is explained as follows.

The greatest reactivity of aminoethylpiperazine in the series of amines studied is due to the presence of piparazine ring. The piparazine ring enhances the electron density at the reaction centre and thereby the electrophile (Cl$^+$) of the oxidant can attacks the reaction centre effectively. The least reactivity of isophoronediamine in the series is due to the presence of cyclohexane ring and steric hindrance exhibited by the groups present in the cyclohexane ring. Among ethylenediamine, diethylenetriamine and triethylenetetramine the reactivity of triethylenetetramine is highest. This may be due to the presence of more (four) amino groups in triethylenetetramine compared to that in diethylenetriamine (three) and ethylenediamine (two). The electron density increases in the chain as the number of amino groups increases and thereby enhances the rate of oxidation. Hence, the order is: triethylenetetramine > diethylenetriamine > ethylenediamine. Overall reactivity was found to be in the order: AEP > TETA > DETA > EDA > IDPA.

The activation energy value is highest for the slowest reaction and vice versa, as expected (Table 3) indicating that the reaction is enthalpy controlled. The isokinetic temperature was calculated by plotting $\Delta H^{\#}$ versus $\Delta S^{\#}$ (Fig. 2; $r = 0.9899$) and the isokinetic temperature $\beta = 385$ K. The genuine nature of the

isokinetic relationship was verified by Exner criterion [39] by plotting log k' (308 K) versus log k' (298 K) (Fig. 2; $r = 0.9824$) and was found to be 370 K. The calculated β value from both the plots are much higher than the temperature range (298–318 K) studied in the present work shows that the reaction is enthalpy
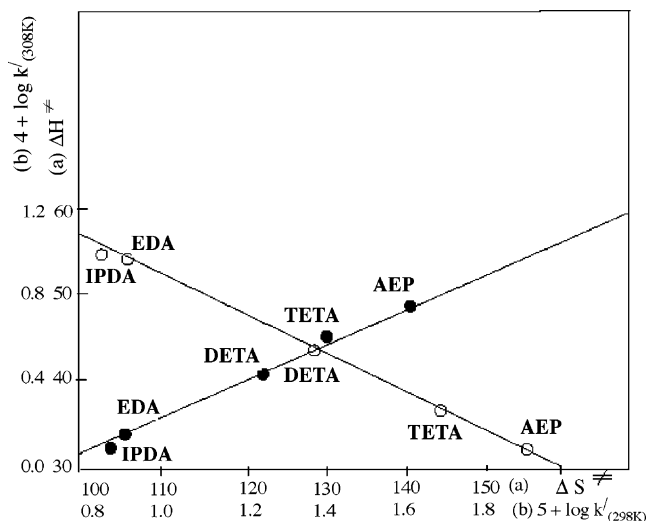
Fig. 2. Isokinetic plots of: (a) $\Delta H^{\#}$ vs. $\Delta S^{\#}$ and (b) log $k'_{(308\,K)}$ vs. log $k'_{(298\,K)}$.
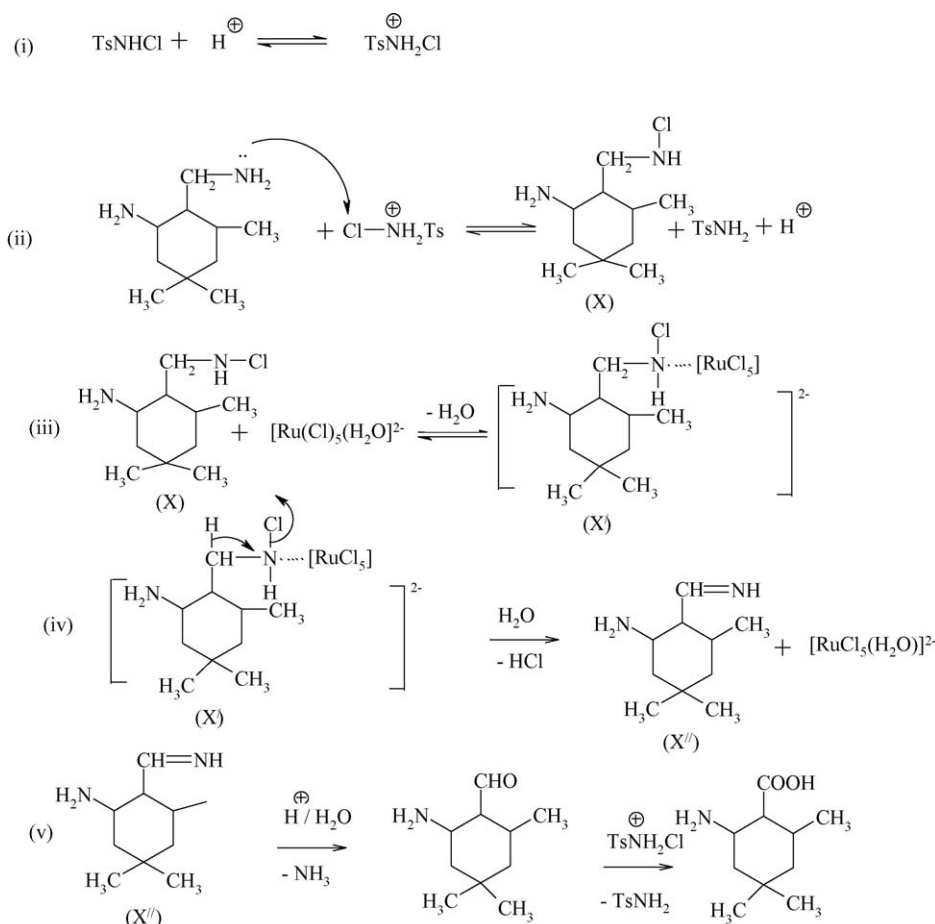
Scheme 6. Oxidation of isophoronediamine by CAT.

controlled. In the literature it is substantiated that for a large number of reactions in which β is higher than the experimental temperature [40–42], the reactions are enthalpy controlled. The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The high positive values of $\Delta G^{\#}$ and $\Delta H^{\#}$ indicate that the transition state is highly solvated. The large negative values of $\Delta S^{\#}$ reflect a more ordered, rigid transition state for each substrate.

2.13. Activation parameters in absence of Ru(III)

It was thought necessary to compare the reactivity of five amines by oxidizing them with CAT in the absence of Ru(III) catalyst under identical experimental conditions. The reactions were studied at different temperatures (298–318 K) and from the plot of $\log k'$ versus $1/T$ ($r > 0.9817$), activation parameters for the uncatalysed reactions were calculated. These data are recorded in Table 3. The rate of oxidation of amines in the absence of Ru(III) catalyst was found to be in the order: AEP > TETA > DETA > EDA > IPDA. A similar trend results in the presence of Ru(III) catalyst also. However, the Ru(III)-catalysed reactions were found to be 2–3-fold faster than the uncatalysed reactions. This was also confirmed by the calculated activation parameters (Table 3). Thus, the observed rates of oxi-

dation obtained in the presence of a micro quantity of Ru(III) justify the use of a catalyst for a facile oxidation of the chosen amines by CAT. The activation parameters evaluated for the catalysed and uncatalysed reactions explains the catalytic effect on the reaction. The catalyst Ru(III) forms the complex (X′) with substrate–oxidant complex (X), which enhances the reducing property of the substrate than that without Ru(III). Further, the catalyst Ru(III) modifies the reaction path by lowering the energy of activation.

2.14. Catalytic activity

It has been pointed out by Moelwyn-Hughes [35] that in presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

$$k_1 = k_0 + K_C[\text{catalyst}]^x \qquad (12)$$

Here, k_1 is the observed pseudo first-order rate constant in the presence of Ru(III) catalyst, k_0 pseudo first-order rate constant for the uncatalysed reaction, K_C the catalytic constant, and x is the order of the reaction with respect to [Ru(III)]. In the present investigations, x values for the standard run were found to be: 0.32 (EDA), 0.30 (DETA), 0.25 (TETA), 0.37 (AEP) and 0.43

Table 4
Values of catalytic constant (K_C) at different temperatures and activation parameters with reference to Ru(III) catalyst calculated using K_C values

Temperature (K)	$10K_C$				
	EDA	DETA	TETA	AEP	IPDA
298	1.48	1.78	1.33	2.20	1.75
303	1.52	1.88	1.49	2.26	1.99
308	1.64	1.93	1.61	2.354	2.18
313	1.86	2.13	1.72	2.50	2.36
318	1.96	2.34	1.83	2.70	2.64
E_a (kJ mol^{-1})	63.62	54.41	47.72	41.86	66.55
$\Delta H^{\#}$ (kJ mol^{-1})	61.03 ± 0.38	51.73 ± 0.49	45.04 ± 0.90	39.22 ± 0.60	63.87 ± 0.60
$\Delta G^{\#}$ (kJ mol^{-1})	50.85 ± 0.67	48.55 ± 0.67	51.19 ± 0.45	46.67 ± 0.79	48.13 ± 0.34
$\Delta S^{\#}$ (J K^{-1} mo^{-1})	−31.39 ± 0.58	−9.36 ± 0.53	−20.30 ± 0.26	−23.30 ± 0.50	−53.87 ± 0.80
Log A	12.5 ± 0.24	11.2 ± 0.10	9.6 ± 0.22	9.40 ± 0.14	13.4 ± 0.10

[CAT]$_0$ = 1.0 × 10^{-3}; [amine]$_0$ = 2.0 × 10^{-2}; [HCl] = 1.0 × 10^{-2} mol dm^{-3}; Ru(III) = 1.0 × 10^{-4} mol dm^{-3}.

(IPDA). Then, the value of K_C is calculated using the equation:

$$K_C = \frac{k_1 - k_0}{[Ru(III)]^x} \qquad (13)$$

The values of K_C were evaluated for each substrate at different temperatures and found to vary at different temperatures. Further, plots of log K_C versus $1/T$ were linear ($r > 0.9822$) and the values of energy of activation and other activation parameters with reference to catalyst were computed. These results are compiled in Table 4.

3. Conclusion

Oxidation of ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), aminoethylpiperazine (AEP) and isophoronediamine (IPDA) by chloramine-T in HCl medium is facile in the presence of a micro quantity of Ru(III) catalyst. The rate of oxidation of amines studied was found to be in the order: AEP > TETA > DETA > EDA > IPDA. The order of reactivity has been explained on the basis of steric and inductive effects. Kinetic behavior of all the substrates are similar and follows the rate law: rate = k[CAT]$_0$[amine]$_0^x$[H$^+$]^y[Ru(III)]^z, where $x, y, z < 1$. Oxidation products were identified. Activation parameters were evaluated for both catalysed and uncatalysed reactions. Catalytic constants and the activation parameters with reference to catalyst were also computed. Ru(III)-catalysed reactions were found to proceed 2–3 times faster than the uncatalysed reactions. In conclusion, it can be said that Ru(III) is an efficient catalyst in the oxidation of the selected amines by CAT in acid medium.

4. Experimental

4.1. Materials

Chloramine-T (Merck) was purified by the method of Morris et al. [17]. An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber colored stoppered bottles until further use. The concentration of stock solutions was periodically determined. Ethylenediamine, diethylenetriamine and triethylenetetramine (SD Fine Chem. Ltd. India), aminoethylpiperazine and isophoronediamine (Aldrich) were of acceptable grades of purity and were used as received. Aqueous solutions of the compounds are employed. A solution of RuCl$_3$ (Merck) in 0.2 mol dm^{-3} HCl was used as the catalyst. Allowance was made for the amount of HCl present in catalyst solution, while preparing solution for kinetic runs. Solvent isotope studies were made in D$_2$O (99.4% purity) supplied by Bhabha Atomic Research Center, Mumbai, India. Reagent grade chemicals and doubly distilled water were used throughout.
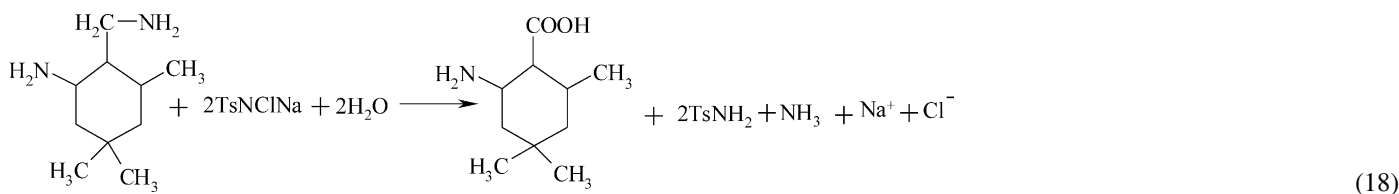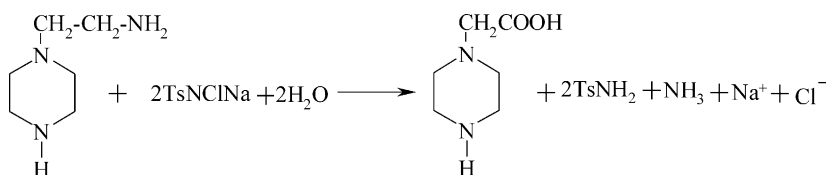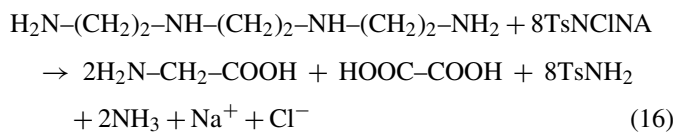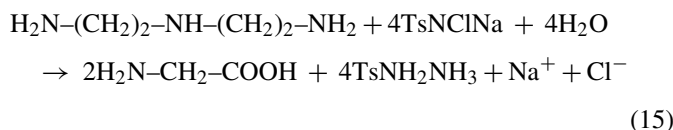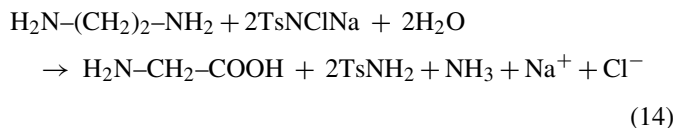
4.2. Kinetic measurements

The reactions were carried out under pseudo first-order conditions by taking a known excess of [substrate]$_0$ over [oxidant]$_0$ at 303 K. The reaction was carried out in stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate photochemical effects. For each run, requisite amounts of solutions of substrate, HCl, RuCl$_3$ and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 303 K until thermal equilibrium was attained. A measured amount of CAT solution, which was also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The course of the reaction was monitored by the iodometric determination of unreacted CAT in 5 ml of aliquots of the reaction mixture withdrawn at different intervals of time. The course of the reaction was studied for at least two half-lives. The pseudo first-order rate constants (k') calculated from the linear plots of log[CAT] versus time were reproducible within ±5%. Regression analysis of experimental data to obtain regression coefficient, r, was performed using an fx-100W scientific calculator.

4.3. Stoichiometry

Stoichiometric investigations revealed that 1 mol of substrate utilized 2 mol of the oxidant in the case of ethelenediamine, aminoethylpiperazine and isophoronediamine, 4 mol in the case

of diethylenetriamine and 8 mol in the case of triethylenete-tramine. The stoichiometric reactions are represented by Eqs. (14)–(18):

$$H_2N–(CH_2)_2–NH_2 + 2TsNClNa + 2H_2O$$
$$\rightarrow H_2N–CH_2–COOH + 2TsNH_2 + NH_3 + Na^+ + Cl^-$$

(14)

$$H_2N–(CH_2)_2–NH–(CH_2)_2–NH_2 + 4TsNClNa + 4H_2O$$
$$\rightarrow 2H_2N–CH_2–COOH + 4TsNH_2NH_3 + Na^+ + Cl^-$$

(15)

$$H_2N–(CH_2)_2–NH–(CH_2)_2–NH–(CH_2)_2–NH_2 + 8TsNClNA$$
$$\rightarrow 2H_2N–CH_2–COOH + HOOC–COOH + 8TsNH_2$$
$$+ 2NH_3 + Na^+ + Cl^-$$

(16)

(17)

(18)

Fig. 3. GC–MS of piperazine-1-acetic acid with its molecular ion peak at 144 amu.

The reduction product of CAT, *p*-toluenesulfonamide (PTS or TsNH$_2$), was detected [10,44] by paper chromatography. Benzyl alcohol saturated with water was used as the solvent with

4.4. Product analysis

The reaction products were neutralized with NaOH and extracted with ether. The organic products were subjected to spot tests and chromatographic analysis which revealed the formation of oxidation products: glycine in the case of ethylenediamine and diethylenetriamine, glycine and oxalic acid in the case of triethylenetetramine, piperazine-1-acetic acid in the case of aminoethylpiperazine and 5-amino-1,3,3,-trimethylycyclohexane-6-carboxylic acid in the case of isophoronediamine. Glycine and oxalic acid [43] were detected by spot tests and comparing them with the authentic samples by TLC analysis. Piperazine-1-acetic acid and 5-amino-1,3,3,-trimethylycyclohexane-6-carboxylic acid were confirmed by GC–MS analysis. GC–MS data was obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectrum was obtained using electron impact ionization technique. The mass spectrum (Fig. 3) showed a molecular peak at 144 amu confirming piperazine-1-acetic acid and molecular ion peak at 185 amu (Fig. 4) confirming 5-amino-1,3,3,-trimethylycyclohexane-6-carboxylic acid. Other peaks observed in the spectra can be interpreted according to the observed structures of the compounds. It was also observed that there was no further oxidation of these products under the present kinetic conditions.
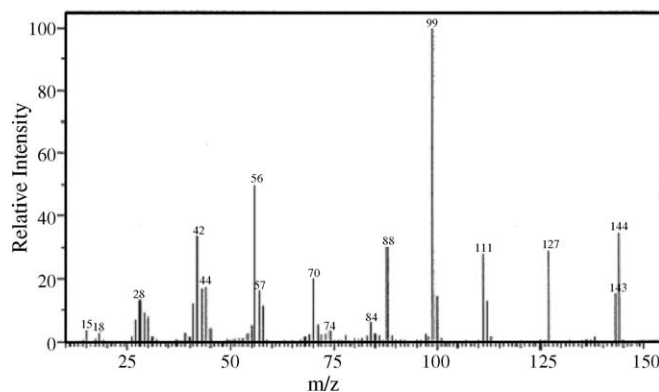
0.5% vanillin in 1% HCl solution in ethanol as spot reagent ($R_f = 0.905$). It was further confirmed by GC–MS analysis. Molecular ion peak of 171 amu clearly confirms PTS (Fig. 5). All the other peaks observed in GC–MS can be interpreted in accordance with the observed structure. The liberated NH$_3$ was identified by Nessler's reagent test.
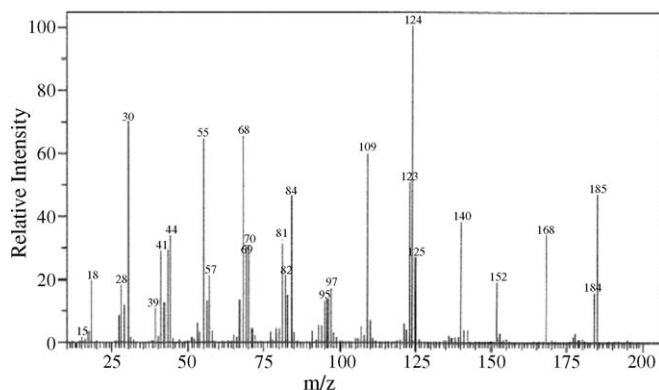

Fig. 4. GC–MS of 5-amino-l,3,3-tiimethylcyclohexane-6-carboxylic acid with its molecular ion peak at 185 amu.
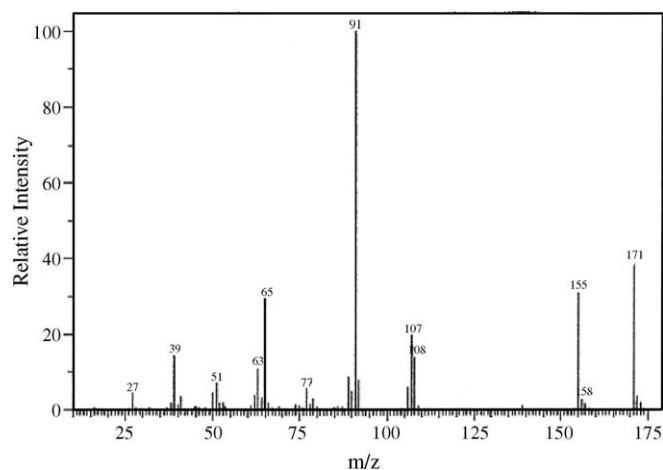
Fig. 5. GC–mass spectrum of *p*-toluenesulfonamide with its molecular ion peak at 171 amu.

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