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Ruthenium complex catalyzed oxidative conversion of aliphatic amines to carboxylic acids using bromamine-T: Kinetic and mechanistic study

C.H. Vinod Kumar[a], K.N. Shivananda[b], Rajenahally V Jagadeesh[c,*], C. Naga Raju[a,*]

[a] *Department of Chemistry, Sri Venkateswara University, SV University Campus, Tirupati 517502, India*
[b] *Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Technion City, Haifa -32000, Israel*
[c] *Division of Organic Chemistry, SSH, VIT University, Vellore-632014, India*

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ABSTRACT

Ruthenium(III) complex catalyzed oxidation of aliphatic amines with bromamine-T under alkaline condition proceeds efficiently to afford carboxylic acids in high conversion. Hexa-coordinated ruthenium(III) complex of the type $[RuCl_2(PPh_3)(L)]$ (L, tridentate ligand derived by the condensation of o-phenylene diamine with salicylaldehyde) has been synthesized and it was used as a catalyst for the oxidative conversion of amines to carboxylic acids. The detailed mechanistic and kinetic investigations have been made for the oxidation reactions. Under similar experimental conditions all the amines proceed with a common oxidation mechanism and follows an identical kinetics with first-order dependence each on $[\text{Oxidant}]_o$ and $[\text{Amine}]_o$, and fractional order with respect to [Catalyst] and $[OH^-]$. To understand the detailed kinetics and mechanism of the reactions, the reactions have been subjected to changes in (i) dielectric permittivity, (ii) primary salt effect, (iii) halide ions and (v) temperature. The reactions were carried out at different temperature and the activation parameters have been calculated. From enthalpy–entropy relationships and Exner correlations, the isokinetic temperature (β) of 382 K, calculated is much higher than the experimental temperature (313 K), indicating that, the enthalpy factor controls the rate. The observed results have been explained by a plausible mechanism and the related rate law has been deduced. The present method developed for the oxidation of amines to carboxylic acids by bromamine-T offers several advantages including high conversion, short reaction times, and stable, cost effective and relatively non-toxic reagents which make the reaction process simple and smooth.

1. Introduction

The oxidation of amines plays a central role in organic chemistry both at the laboratory and industry level. Several methods [1–6] are available to effect the oxidation, and continuous attention is drawn to newer and more selective methods of amine oxidation. Different methods were designed to give different oxidation products in the amine oxidation [1–6]. 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 presented [6]. The amines selected for the oxidation-kinetic studies are ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), bishexamethylenetriamine (BHMT), 2-methylpentamethyldiamine (2-MPDA) and 2,2,4-trimethyldiamaine (2,2,4-TMHDA). Catalytic oxidation with haloamine such as bromamine-T is particularly attractive from an economic and environmental point of view. The development of new processes for the selective oxidations with environmentally friendly oxidants has potential practical applications in organic synthesis. In this regard, we used sodium N-bromo-p-toluene sulfonamide or bromamine-T ($p\text{-}CH_3C_6H_4SO_2NBrNa{\cdot}3H_2O$; abbreviated as BAT), a member of organic haloamine as an oxidant in NaOH medium for the selective oxidative conversion of aliphatic amines to carboxylic acids using hexa-coordinated ruthenium complex as catalyst with a view to explore the detailed mechanistic and kinetic aspects of the reactions.

The chemistry of N-metallo-N-arylhalosulfonamides, generally known as organic haloamines, is of interest due to their diverse behaviour. Their versatile nature is due to their ability to act as sources of halonium cations, hypohalite species and nitrogen anions. The monohaloamines are two-electron change oxidants while dihaloamines undergo four-electron changes. As a result, these compounds react with a range of functional groups and affect a variety of molecular changes. The prominent member of this group is chloramine-T (CAT), which contains chlorine in +1 oxidation state and is a by-product in the manufacture of saccharin.

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* Corresponding authors.
E-mail addresses: rvjdeesh@yahoo.com (R.V. Jagadeesh), chvinod20@yahoo.com (C.N. Raju).

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Bromamine-T (p-$MeC_6H_4SO_2NBrNa{\cdot}3H_2O$ or TsNBrNa or BAT), the bromine analogue of CAT, is gaining importance as a mild oxidant and is found to be a better oxidizing agent than the chloro compound. It can be easily prepared from chloramine-T. Although the mechanistic aspects of many of the haloamine reactions have been well documented [7–12], similar studies on bromine analogues are sparse. In view of these facts, there is a considerable scope for the study with BAT to get a better insight of the speciation of BAT reaction models and to understand its redox chemistry in solutions.

Ruthenium has various valences (0–8 valences) and is not so expensive transition metal; therefore, various useful catalytic reactions for organic synthesis have been explored [13]. It is noteworthy that the medical property of ruthenium is now being recognized, and ruthenium anticancer agents have recently entered the clinic, showing promising activity on resistant tumors. There has been considerable interest in ruthenium complexes in recent years because of their redox stability [14]. Metal complexes of ruthenium containing nitrogen and oxygen donor ligands are found to be effective catalysts for oxidation, reduction, hydrolysis, and other organic transformations [15–16]. In the present work, we have chosen a ruthenium complex with group of three tridentate O, N, N donor ligands. The ligand is abbreviated in general as L. The ligand has three potential donor sites, viz., a phenolate oxygen, an azomethine nitrogen and an amine nitrogen.

The applications in the oxidative conversion of amines to carboxylic acids and the usefulness of ruthenium catalysis in organic reactions instigate us to carryout the title reaction to develop a protocol for the oxidation of amines with an interest of studying the oxidation mechanism with kinetic interpretations. The main objectives of the present investigation are to: (i) develop an appropriate experimental condition for the oxidation process, (ii) study the catalytic activity of catalyst, (iii) elucidate plausible mechanism, (iv) deduce appropriate rate law and (v) ascertain the various reactive species.

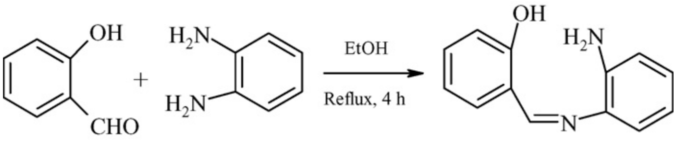
2. Experimental

2.1. Preparation of oxidant

Bromamine-T was prepared [17] using chloramine-T. To a solution of CAT (20 g in 400 mL of water), about 4 mL of liquid bromine was added drop wise with constant stirring at room temperature to yield dibromamine-T (DBT). The solid DBT was filtered under suction, washed thoroughly with ice cold water until all the absorbed bromine was removed and then vacuum-dried for 24 h. About 20 g of DBT thus obtained was dissolved in 30 mL of 4 mol dm^{-3} NaOH with constant stirring at room temperature and the resultant aqueous solution was cooled in ice. Pale yellow crystals of BAT formed was filtered under suction, washed quickly with the minimum amount of ice cold water and dried over P_2O_5. Aqueous solution of the oxidant was standardized by iodometric procedure and preserved in brown bottles to prevent photochemical deterioration.

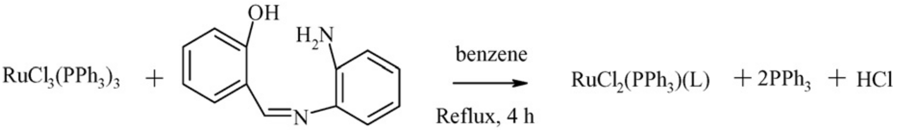
2.2. Preparation of catalyst

The Schiff's base ligand was prepared by the reaction between salicylaldehyde and o-phenylene diamine. Ethanolic solutions of salicylaldehyde (0.01 mol) in 20 mL and o-phenylenediamine (0.01 mol) in 20 mL were mixed and refluxed for about 4 h. The reaction mixture was evaporated to a small volume and left to cool. The resulting Schiff's base ligand precipitated on cooling and then was it filtered off, washed with ethanol and recrystallized from ethanol. The purity of the Schiff's base ligand was monitored on TLC using eluants 1:1 ethyl acetate and petroleum ether and separated by column chromatography (yield = 90%). The ligand was characterized by FT-IR spectral analysis. IR spectra of Schiff's base showed a strong band around 1580–1600 cm^{-1} for the free azomethine (—CH=N—) group. In the complex, this band is shifted to the region 1522–1543 cm^{-1}, indicating the coordination of the Schiff's base through the azomethine nitrogen [18]:



(1)

The starting complex $[RuCl_3(PPh_3)_3]$ was prepared according to the reported literature procedures [19]. The ruthenium complex was prepared by the reaction between $[RuCl_3(PPh_3)_3]$ and Schiff's base. The mixture (1:1 ratio) of $[RuCl_3(PPh_3)_3]$ (0.1 mmol) and Schiff's base ligand (0.1 mmol) in 20 mL benzene was heated under reflux for 5 h. After completion of the reaction, the reaction mixture was concentrated and cooled to room temperature followed by the addition of ether. The solid complex was removed by filtration, washed with petroleum ether, recrystallized from CH_2Cl_2 and dried in vacuum. The yield of the complex is found to be around 70%:



(2)

The complex was characterized spectroscopically as follows.

Strong band was observed in the region 1270–1300 cm^{-1} for free Schiff's base has been assigned to phenolic C—O stretching. After the complexation, this band was shifted to higher frequency region 1290–1330 cm^{-1}, indicates that the other coordination is through the phenolic oxygen atom [20]. The characteristic absorption band for primary amine N—H stretching is observed in the region 3450–3500 cm^{-1}. In the spectra of the new ruthenium(III) complex, the absorptions due to the —NH_2 group has been observed at a lower region 3400–3470 cm^{-1}, indicating that the other coordination site is amine nitrogen atom to the metal ion [21]. The other characteristic bands due to triphenylphosphine were also present in the expected region. Elemental analysis of the complex was also made and the percentage of carbon, hydrogen and nitrogen were found to be 58.25, 4.62 and 4.46 respectively.

The electronic spectrum of ruthenium(III) complex showed charge transfer bands [22]. Due to the relatively high oxidizing properties of ruthenium(III), the charge transfer bands of type $L_{\prod y} \rightarrow t_{2g}$ are prominent in the lower energy region. The electronic spectrum of the complex is showed in the 360 nm region.

The EPR spectrum (Fig. 1) in solid state at X-band frequencies of ruthenium(III) complex was recorded at room temperature. The complex showed a single isotropic line with g value in the 2.34–2.44 range (Fig. 1). This type of isotropic lines is observed due to intramolecular spin exchange.

Based on the above spectroscopic data the complex is hexacoordinated, with the donor atoms distributed about the metal center in an octahedral fashion as shown in Fig. 2.

Ethylenediamine, diethylenetriamine and triethylenetetramine (SD Fine Chem. Ltd. Ind.), tetraethylenepentamine, bishex-

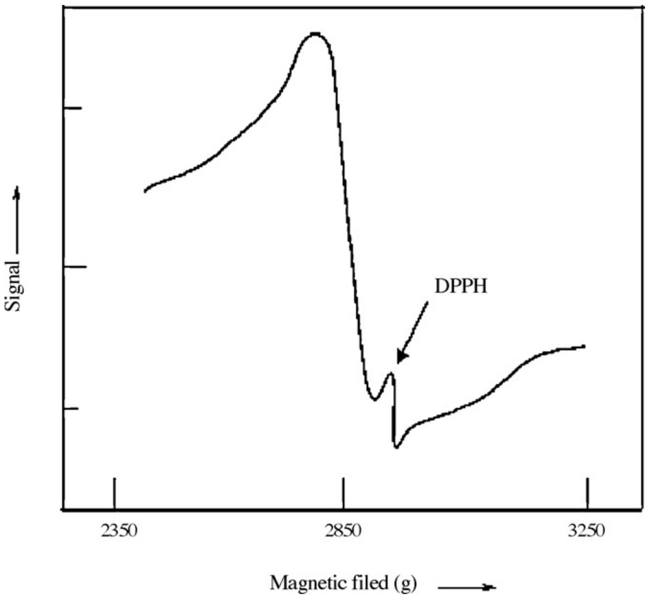


Fig. 1. EPR spectrum of complex $[RuCl_2(PPh_3)(L)]$.

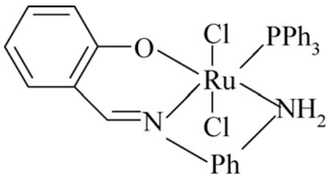


Fig. 2. Structure of complex $RuCl_2(PPh_3)(L)$.

amethylenetriamine, 2-methylpentamethyldiamine and 2,2,4-trimethyldiamaine (Aldrich) were of acceptable grades of purity and were used as received. Aqueous solutions of these compounds in 0.001 mol dm^{-3} HCl are employed. A solution of ruthenium(III) complex in 0.02 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_2O (99.4% purity) supplied by Bhabha Atomic Research Center, Mumbai, India. Reagent grade chemicals and doubly distilled water were used throughout the experiments.

2.3. Kinetic measurements

The reactions were carried out under pseudo first-order conditions by taking a known excess of $[\text{Amine}]_o$ over $[\text{oxidant}]_o$ at 313 K. The reaction was carried out in stoppered Pyrex boiling tubes whose outer surfaces were coated with black to eliminate photochemical effects. For each run, requisite amounts of solutions of substrate, NaOH, Ru(III) complex and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 313 K until thermal equilibrium was attained. A measured amount of BAT 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 BAT 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 [BAT] vs. time were reproducible within ±5%. Regression analysis of experimental data to obtain regression coefficient, r, was performed using a fx-100W scientific calculator.

3. Results

3.1. Oxidation of amines

Selective oxidation of amines to carboxylic acids was made with bromamine-T oxidant in alkaline medium in presence of catalytic amount of ruthenium(III) complex. Stoichiometry of each amine oxidation was determined by equilibrating each amine with excess of oxidant in presence of 0.01 mol dm^{-3} NaOH and 1.0×10^{-4} mol dm^{-3} catalyst at 313 K for 48 h. Determination of the unreacted BAT reveals the stoichiometry (amine:oxidant) of each amine oxidation reaction and the results were presented in Table 1. Oxidation of amines was achieved by stirring 1 mmol of amine with stoichiometric amount of oxidant in presence of 0.01 mmol of ruthenium catalyst and 0.1 mmol NaOH medium at 313 K. After completion of the reaction (monitored by TLC), the reaction products were neutralized by acid and extracted with ether. The organic products were subjected to GC-Mass analysis and products were characterized by mass spectral analysis. The oxidation products obtained and stoichiometry of the reactions were presented in Table 1.

3.2. Kinetics of oxidation of amines

The kinetics of oxidation of amines by BAT were investigated at several initial concentrations of the reactants in alkaline medium. With the substrate in excess, at constant [NaOH], $[\text{Amine}]_o$ and temperature, plots of log [BAT] vs. time were linear ($r > 0.9976$) indicating a first-order dependence of rate on $[\text{BAT}]_o$. The values of pseudo first-order rate constants (k') are given in Table 2. Further,

Table 1
Ruthenium complex catalyzed oxidative conversion of amines to carboxylic acids usingbromamine-T in NaOH medium.

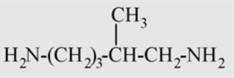
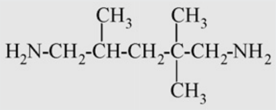
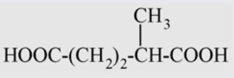
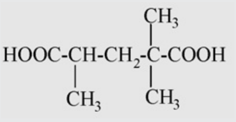
Entry	Amine	Product(s)	Stoichiometry (Amine:BAT)	Conversion (%)
A	$H_2N\text{-}(CH_2)_2\text{-}NH_2$	$H_2N\text{-}CH_2\text{-}COOH$	1:2	88
B	 $H_2N\text{-}(CH_2)_3\text{-}\overset{\overset{CH_3}{\vert}}{C}H\text{-}CH_2\text{-}NH_2$	 $H_2N\text{-}CH_2\text{-}\overset{\overset{CH_3}{\vert}}{C}H\text{-}CH_2\text{-}\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}\text{-}CH_2\text{-}NH_2$	1:4	89
C	 $HOOC\text{-}(CH_2)_2\text{-}\overset{\overset{CH_3}{\vert}}{C}H\text{-}COOH$	 $HOOC\text{-}\underset{\underset{CH_3}{\vert}}{C}H\text{-}CH_2\text{-}\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}\text{-}COOH$	1:4	88
D	$H_2N\text{-}(CH_2)_6\text{-}NH\text{-}(CH_2)_6\text{-}NH_2$	$2HOOC\text{-}(CH_2)_4\text{-}COOH$	1:7	90
E	$H_2N\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH_2$	$2H_2N\text{-}CH_2\text{-}COOH$	1:7	92
F	$H_2N\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH_2$	$2H_2N\text{-}CH_2\text{-}COOH + HOOC\text{-}COOH$	1:8	90
G	$H_2N\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH_2$	$3H_2N\text{-}CH_2\text{-}COOH + HOOC\text{-}COOH$	1:10	91

Table 2
Effect of varying reactant concentrations on the reaction rate.

10^3 $[BAT]_o$ (mol dm^{-3})	10^2 $[Amine]_o$ (mol dm^{-3})	10^4 k' (s^{-1})						
		A	B	C	D	E	F	G
0.25	1.00	3.20	4.10	5.20	7.0	7.90	10.3	12.1
0.50	1.00	3.15	4.00	5.15	6.8	7.75	10.2	12.2
1.00	1.00	3.10	4.20	5.10	6.9	7.85	10.4	12.0
2.00	1.00	3.16	4.30	5.21	6.85	7.90	10.1	11.9
4.00	1.00	2.96	4.15	4.95	7.01	7.95	10.5	12.1
1.00	0.25	0.75	1.02	1.30	1.70	2.00	2.7	3.10
1.00	0.50	1.50	2.11	2.60	3.50	4.00	5.20	6.05
1.00	1.00	3.10	4.20	5.10	6.9	7.85	10.4	12.0
1.00	2.00	6.24	8.42	10.2	14.0	15.9	20.9	24.1
1.00	4.00	12.6	17.0	20.6	28.0	31.2	42	48.4

$[NaOH] = 1.0 \times 10^{-2}$ mol dm^{-3}; $Ru(III) = 1.0 \times 10^{-5}$ mol dm^{-3}; $T = 313$ K

Table 3
Effect of varying NaOH and Ru(III) concentrations on the reaction rate.

10^2 [NaOH] (mol dm^{-3})	10^5 [Ru(III)] (mol dm^{-3})	10^4 k' (s^{-1})						
		A	B	C	D	E	F	G
0.25	1.00	1.41	1.90	2.35	2.99	3.61	4.51	5.55
0.50	1.00	2.10	2.85	3.41	4.51	5.41	7.00	8.4
1.00	1.00	3.10	4.20	5.10	6.9	7.85	10.4	12.0
2.00	1.00	4.51	6.31	7.62	10.0	11.9	15.2	18.6
4.00	1.00	6.85	9.21	11.3	14.4	17.8	22.4	28.1
1.00	0.25	1.00	1.31	1.70	2.39	2.91	3.59	4.31
1.00	0.50	1.81	2.40	3.02	4.01	4.79	6.10	7.51
1.00	1.00	3.10	4.20	5.10	6.9	7.85	10.4	12.0
1.00	2.00	5.31	7.10	8.91	11.5	13.8	17.8	21.8
1.00	4.00	8.90	12.0	14.8	20.0	23.0	29.0	37.0

$[BAT]_o = 1.00 \times 10^{-3}$; $[Amine]_o = 1.00 \times 10^{-2}$; $T = 313$ K.

the values of k' are unaffected with variation of $[BAT]_o$, confirming first-order dependence on $[BAT]_o$. The rate increases with increase in $[Amine]_o$ (Table 2) and plot of log k' vs. log [Amine] were linear ($r > 0.9909$) with unit slope indicating first-order dependence of rate on $[Amine]_o$. The rate of reaction increases with increase in [NaOH] (Table 3) and plots of log k' vs. log [NaOH] were linear ($r > 0.9909$) with slopes of 0.5–0.55 indicating fractional-order dependence of rate on [NaOH]. Further, the rate of the reaction increases with increasing [Ru(III)] (Table 3) and a plots of log k' vs. log [Ru(III)] were linear ($r > 0.9957$) with slopes less than unity (0.7–0.75) indicating a fractional-order dependence of rate on [Ru(III)].

Addition of p-toluenesulfonamide (PTS or $TsNH_2$) and halide ions, Cl^- or Br^- ions, in the form of NaCl or NaBr (1–10×10^{-3} mol dm^{-3}) or variation of the ionic strength (I) of medium using $NaClO_4$ solution (0.1–0.5 mol dm^{-3}) showed negligible effect on the rate. The dielectric constant of the solvent medium was varied by adding methanol (0–30%, v/v), which had negative influence on the rate (Table 4). Solvent isotope studies in D_2O medium (0–100%) with ethylenediamine as a probe gave the values: $k'(H_2O) = 3.10 \times 10^{-4}$ s^{-1} and $k'(D_2O) = 3.88 \times 10^{-4}$ s^{-1}. The solvent isotope effect $k'(H_2O)/k'(D_2O) = 0.81$ indicates a slight increase of rate in D_2O medium.

Table 4
Effect of varying dielectric constant (D) of the medium on the rate of reaction.

%MeOH (v/v)	D	10^4 k' (s^{-1})						
		A	B	C	D	E	F	G
0.0	76.73	3.10	4.20	5.10	6.90	7.85	10.4	12.0
10.0	72.37	2.81	3.61	4.41	5.71	6.71	8.70	10.9
20.0	67.48	2.41	3.20	3.80	5.00	5.80	7.41	8.91
30.0	62.71	2.00	2.70	3.11	4.10	4.61	5.91	7.11

$[BAT]_o = 1.0 \times 10^{-3}$; $[Amine]_o = 1.0 \times 10^{-2}$; $[NaOH] = 1.0 \times 10^{-2}$ mol dm^{-3}; $Ru(III) = 1.0 \times 10^{-5}$ mol dm^{-3}; $T = 313$ K.

The reactions were carried out in a range of temperature 303–323 K, keeping other experimental conditions constant. From the linear Arrhenius plot of log k vs. log$(1/T)$ ($r = 0.9901$), values of composite activation parameters E_a, $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ were evaluated. These results are summarized in Table 5. Addition of reaction

Table 5
Temperature dependence on the reaction rate and values of composite activation parameters for the oxidation of amines by BAT.

Temperature (K)	10^4 k' (s^{-1})						
	A	B	C	D	E	F	G
303	0.90	1.20	1.80	2.50	3.20	4.50	5.50
308	1.80	2.20	3.00	4.00	5.00	6.40	9.00
313	3.10	4.20	5.10	6.90	7.85	10.4	12.0
318	6.20	8.00	9.50	11.0	13.0	15.0	17.1
323	12.4	14.0	18.1	20.0	22.0	27.1	29.0
E_a (kJ mol^{-1})	100	93.7	83.7	77.4	71.1	62.7	56.5
$\Delta H^{\#}$ (kJ mol^{-1})	97.5	90.8	80.7	74.5	68.2	59.8	53.3
$\Delta G^{\#}$ (kJ mol^{-1})	98.2	97.5	96.8	95.5	95.0	94.5	94.0
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−5.00	−18.8	−49.0	−62.7	−87.0	−110	−129

$[BAT]_o = 1.0 \times 10^{-3}$; $[Amine]_o = 1.0 \times 10^{-2}$; $[NaOH] = 1.0 \times 10^{-2}$ mol dm^{-3}; $Ru(III) = 1.0 \times 10^{-5}$ mol dm^{-3}.

mixture to acrylamide in an inert atmosphere did not initiate polymerization of the latter showing the absence of any free radical in the reacting system.

4. Discussion

4.1. Reactive species of oxidant

Pryde and Soper [23], Morris et al. [24] and Bishop and Jennings [25] have shown the existence of similar equilibria of N-metallo-N-arylhalosulfonamides in aqueous media. Bromamine-T, like CAT acts as an oxidizing agent in both acidic and alkaline solutions. The oxidation potential of BAT/$TsNH_2$ is pH dependent and decreases with increase in the pH of the solution with 1.14 V at pH 0.65 and 0.50 V at pH 12. Depending on the pH, BAT exhibits the following equilibria in aqueous solutions [23–26].

$$TsNBrNa \rightleftharpoons TsNBr^- + Na^+ \quad (3)$$

$$TsNBr^- + H^+ \rightleftharpoons TsNHBr \quad (4)$$

$$2TsNHBr \rightleftharpoons TsNH_2 + TsNBr_2 \quad (5)$$

$$TsNHBr + H_2O \rightleftharpoons TsNH_2 + HOBr \quad (6)$$

$$TsNBr_2 + H_2O \rightleftharpoons TsNHBr + HOBr \quad (7)$$

$$HOBr \rightleftharpoons H^+ + OBr^- \quad (8)$$

$$HOBr + H^+ \rightleftharpoons H_2OBr^+ \quad (9)$$

where Ts = p-$CH_3C_6H_4SO_2$.

The possible oxidizing species in acidified BAT solutions are TsNHBr, $TsNBr_2$ HOBr and possibly H_2OBr^+ and possible oxidizing species in alkaline medium would be $TsNBr^-$ and OBr^- anions. These anionic species were transformed into more reactive species, TsNHBr and HOBr during the course of the reaction in alkaline and acidic media. Several workers have observed the retarding effect of OH^- ions on the rate of haloamines with a number of substrates [27–30] and have suggested that the reactivity of weakly alkaline solutions of haloamines is due to the formation of the conjugate acid TsNHBr from $TsNBr^-$ in OH^- retarding step. But in the present investigations, the OH^- ions increases the rate of the reaction clearly indicates $TsNBr^-$ is the reactive oxidizing species. In earlier work [31–33] the positive influence of OH^- ion on the rate of haloamine reactions with a number of substrates have been observed and suggested RNX^- (R = Ts or $PhSO_2$; X = Cl or Br) is the reactive oxidizing species. In the present investigations, rate of the reaction is accelerated by OH^- ions clearly indicates that the anion $TsNBr^-$ is the significant oxidizing species involved in the oxidation of FA by BAT in all the four catalyzed reactions.

$$\begin{array}{llll}
TsNHBr + OH^- & \overset{K_1}{\rightleftharpoons} & TsNBr^- + H_2O & \text{(i) fast} \\
TsNBr^- + Ru(III) & \overset{K_2}{\rightleftharpoons} & X & \text{(ii) fast} \\
X + Amine & \xrightarrow{k_3} & X' & \text{(iii) slow and rds} \\
X' + n\,TsNBr^- & \xrightarrow{k_4} & Products & \text{(iv) fast}
\end{array}$$

Scheme 1.

4.2. Mechanism and rate law for the oxidation of amines

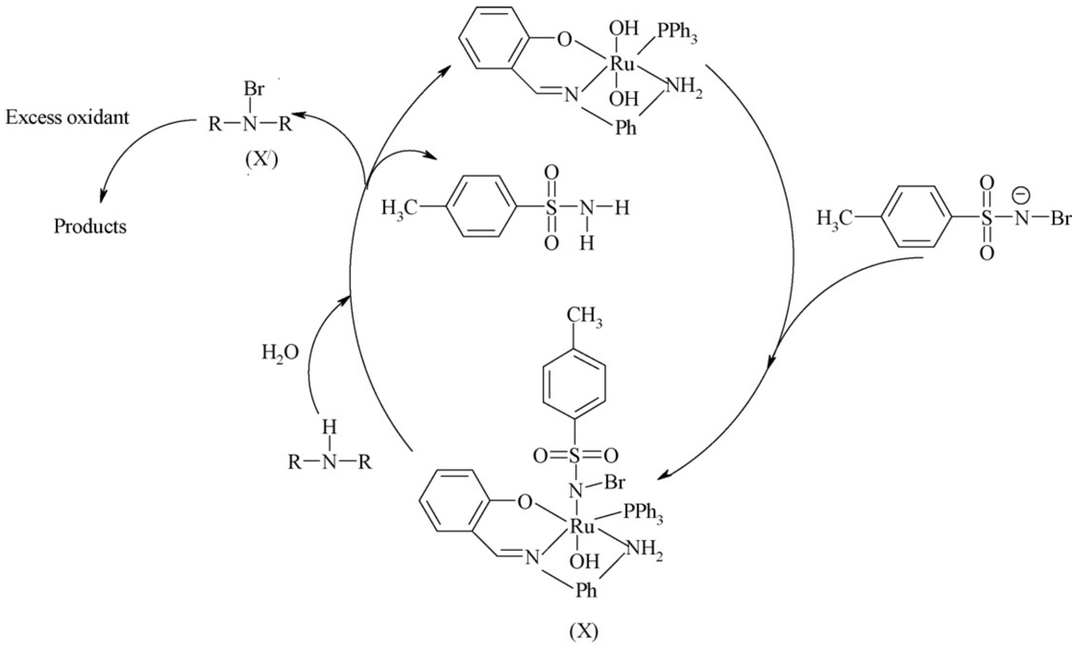
Under the experimental conditions, $[OH^-] \gg [Ru(III)]$ and the fact that $[OH^-]$ increases the rate, ruthenium(III) is mostly present as the hydroxylated species $[Ru(OH)_2(PPh_3)(L)]$ and its formation is given in the following equilibrium:

$$[RuCl_2(PPh_3)(L)] + 2OH^- \rightleftharpoons [Ru(OH)_2(PPh_3)(L)] + 2Cl^- \quad (10)$$

The existence of intermediate between Ru(III) and oxidant was evidenced from the UV–vis spectra of both Ru(III) and Ru(III)-BAT mixture, in which a shift of Ru(III) from 360 to 350 nm was observed, indicating the intermediate species between catalyst and oxidant.

Based on the above discussion and the observed kinetic results, mechanism as shown in Scheme 1 is proposed for the ruthenium catalyzed oxidation of amines by BAT in alkaline medium.

In Scheme 1, X and X′ present the intermediate species whose structures are shown in Scheme 2. The detailed mechanism of ruthenium complex catalyzed oxidative conversion of amines is shown in Scheme 2.



Scheme 2.

The total effective concentration of BAT is:

$$[\mathrm{BAT}]_t = [\mathrm{TsNHBr}] + [\mathrm{TsNBr}^-] + [\mathrm{X}] \tag{11}$$

By substituting for [TsNHBr] and $[\mathrm{TsNBr}^-]$ from steps of (i) and (ii) of Scheme 1 in Eq. (11) and solving for [X], we get:

$$[\mathrm{X}] = \frac{K_1K_2[\mathrm{BAT}]_t[\mathrm{Ru(III)}][\mathrm{OH}^-]}{[\mathrm{H_2O}] + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{Ru(III)}][\mathrm{OH}^-]} \tag{12}$$

From the slow step of Scheme 1:

$$\mathrm{rate} = -\mathrm{d}[\mathrm{BAT}]_t/\mathrm{d}t = k_3[\mathrm{X}][\mathrm{Amine}] \tag{13}$$

By substituting for [X] from Eq. (12) into Eq. (13), the following rate law was obtained:

$$\mathrm{rate} = \frac{K_6K_7k_8[\mathrm{BAT}]_t[\mathrm{Amine}][\mathrm{Ru(III)}][\mathrm{OH}^-]}{[\mathrm{H_2O}] + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{Ru(III)}][\mathrm{OH}^-]} \tag{14}$$

Scheme 1 and the rate law (14) are consistent with the observed experimental results and supported by the following facts.

For reaction involving fast pre-equilibrium H^+ or OH^- ion transfer, the rate increases in $\mathrm{D_2O}$ since $\mathrm{D_3O}^+$ and OD^- are 2–3 times stronger acids and stronger bases [34,35], respectively, than $\mathrm{H_3O}^+$ and OH^- ions. In the present studies the observed solvent isotope effect of $k'(\mathrm{H_2O})/k'(\mathrm{D_2O}) < 1$ is due to the greater basicity of OD^- compared to OH^-. The magnitude of increase of rate in $\mathrm{D_2O}$ is small ($k'(\mathrm{H_2O})/k'(\mathrm{D_2O}) = 0.81$) compared to the expected value of 2–3 times greater, which can be attributed to the fractional-order dependence of rate on $[\mathrm{OH}^-]$. The negligible influence of variation of the ionic strength and addition of PTS and halide ions on the rate of the reaction and also activation parameters are in good agreement with the mechanism proposed and the rate law derived.

A decrease in the rate with a decrease in D of the medium supports the proposed mechanism. Amis and Jaffe [36] have shown that:

$$\log k'_D = \log k' + \frac{Ze\mu}{2.303kTr^2D} \tag{15}$$

where k'_D is a function of dielectric constant D, Ze is the charge on the ion, μ is the dipole moment of the dipole, k is the Boltzmann constant, T is the absolute temperature and r is the distance of approach between the ion and dipole. Eq. (15) predicts a linear relation between $\log k'$ vs. $\log(1/D)$. The slope of the line should be negative for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope is obtained for positive ion–dipole reactions. In the present investigations, plots of $\log k'$ vs. $\log(1/D)$ were linear with negative slopes, supporting the participation of negative ion and dipole in the rate-limiting step (Scheme 1).

The activation energy value is highest for the slowest reaction and vice versa (Table 5) indicating that the reaction is enthalpy controlled. Further, values of $\Delta H^{\#}$ and $\Delta S^{\#}$ can be correlated linearly ($r = 0.9985$) resulting in an isokinetic relation, which indicates that a common mechanism operates in the oxidation of the selected amines by BAT. The slope gives the value of the isokinetic temperature (β) as 382 K. Furthermore, verification of existence of isokinetic relationship has been done by Exener criterion [37] by plotting $\log k'_{(313\,\mathrm{K})}$ vs. $\log k'_{(303\,\mathrm{K})}$ which is linear ($r = 0.9919$). The β value was calculated using the equation $\beta = T_1T_2(1-q)/(T_1 - T_2q)$ where q is the slope of the Exener plot; β was found to be 380 K. The calculated β value from both the plots are much higher than the temperature range (303–323 K) employed in the present work and shows that the reaction is 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 negative values of $\Delta S^{\#}$ indicate a more ordered, rigid transition state for each substrate. Consistent values of $\Delta G^{\#}$ is in favor of common mechanism operates for all the amine oxidation reactions.

5. Conclusions

Oxidative conversion of aliphatic amines to carboxylic acids was achieved efficiently using bromamine-T oxidant with Ru(III) complex catalyst. Hexa-coordinated ruthenium complex was prepared and used and its catalytic efficiency was observed in the amine oxidation. All the seven reactions followed identical kinetics with similar mechanism operation Activation parameters and isokinetic temperature were deduced. The reactions were carried out at different temperatures and the activation parameters were evaluated for each reaction. The present method developed for the oxidation of amines to carboxylic acids by BAT offers several advantages including good conversion, short reaction times, and stable, cost effective and relatively non-toxic reagents which make the reaction process simple and smooth. The observed results have been explained by a plausible mechanism and the related rate law has been deduced. It can be concluded that Ru(III) complex/bromamine-T system effectively performs the oxidative conversion of amines in alkaline medium.

References

[1] J. Schmidt, H.J. Schäfer, Angew. Chem. Int. Ed. 20 (1981) 109.
[2] S.M. Samec, A.H. Éll, J.E. Bäckvall, Chem.: Eur. J. 11 (2005) 2327.
[3] R. Saxena, A. Shukla, S.K. Upadhyay, Trans. Met. Chem. 19 (1994) 91.
[4] J. Matsuo, A. Kawana, Y. Fukuda, T. Mukaiyama, Chem. Lett. 30 (2001) 712.
[5] S. Ananda, M.B. Jagadeesha, Puttaswamy, B.M. Venkatesha, T.K. Vinod, N.M.N. Gowda, Int. J. Chem. Kinet. 32 (2000) 776.
[6] I.P. Gragerov, L.K. Skrunts, B.A. Geller, Russ. Chem. Rev. 51 (1982) 68.
[7] Puttaswamy, R.V. Jagadeesh, N.M.M. Gowda, Int. J. Chem. Kinet. 35 (2005) 700.
[8] V.R.S. Rao, D. Venkappayya, G. Aravamudan, Talanta 17 (1970) 770.
[9] M.M. Campbell, G. Johnson, Chem. Rev. 78 (1978) 65.
[10] D.H. Bremner, Synth. Reagents 6 (1985) 9.
[11] K.K. Banerji, B. Jayaram, D.S. Mahadevappa, J. Sci. Ind. Res. 46 (1987) 65.
[12] K.S. Rangappa, H. Ramachandra, D.S. Mahadevappa, N.M. Made Gowda, Int. J. Chem. Kinet. 28 (4) (1996) 265.
[13] B. Bosnich, Aldrich. Chim. Acta 31 (1998) 76.
[14] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Chem. Rev. 96 (1996) 759.
[15] R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan, Inorg. Chem. Commun. 6 (2003) 486.
[16] R. Ramesh, Inorg. Chem. Commun. 7 (2004) 274.
[17] C.G.R. Nair, R.L. Kumari, P. Indrasenan, Talanta 25 (1978) 525.
[18] B. Khera, A.K. Sharma, N.K. Kaushik, Polyhedron 2 (1983) 1177.
[19] J. Chatt, G. Leigh, D.M.P. Mingos, R.J. Paske, J. Chem. Soc. A (1968) 2636.
[20] R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan, Inorg. Chem. Commun. 5 (2002) 487.
[21] D.M. Boghaei, S. Mohebi, J. Mol. Catal. A: Chem. 179 (2002) 41.
[22] A.B.P. Lever, Electronic Spectra of d^n ions in Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, New York, 1984, p. 376.
[23] B.G. Pryde, F.G. Soper, J. Chem. Soc. (1931) 1510.
[24] J.C. Morris, J.A. Salazar, M.A. Wineman, J. Am. Chem. Soc. 70 (1948) 2036.
[25] E. Bishop, V.J. Jennings, Talanta 1 (1958) 197.
[26] F.F. Hardy, J.P. Johnston, J. Chem. Soc.: Perkin Trans. II (1973) 742.
[27] D.S. Mahadevappa, K.S. Rangappa, N.M.M. Gowda, B.T. Gowda, Int. J. Chem. Kinet. 14 (1982) 1183.
[28] S. Meenakshisundaram, R.M. Sockalingam, J. Mol. Catal. A: Chem. 160 (2000) 269.
[29] Puttaswamy, R.V. Jagadeesh, Cent. Eur. J. Chem. 3 (3) (2005) 482.
[30] M.H. Kondarasaiah, S. Ananda, Puttaswamy, N.M.M. Gowda, Synth. React. Inorg. Met-Org. Chem. 33 (7) (2003) 1145.
[31] Ramalingaiah, R.V. Jagadeesh, Puttaswamy, Catal. Commun. 9 (2008) 1443.
[32] Puttaswamy, R.V. Jagadeesh, Int. J. Chem. Kinet. 37 (2005) 201.
[33] Puttaswamy, R.V. Jagadeesh, Ind. Eng. Chem. Res. 45 (2006) 1563.
[34] C.J. Collins, N.S. Bowman, Isotope Effects in Chemical Reactions, Van Nostrand Reinhold, New York, 1970, p. 267.
[35] K.B. Wiberg, Chem. Rev 55 (1955) 713;
K.B. Wiberg, Physical Organic Chemistry, Wiley, New York, 1964.
[36] E.S. Amis, G. Jaffe, J. Chem. Phys. 10 (1942) 598.
[37] O. Exner, Collect. Czech. Chem. Commun. 29 (1964) 1095.