Journal of Molecular Catalysis A: Chemical 328 (2010) 99–107

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Development of an efficient ruthenium catalyzed synthetic process and mechanism for the facile conversion of benzothiazoles to orthanilic acids

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ARTICLE INFO

Article history:
Received 10 March 2010
Received in revised form 2 June 2010
Accepted 4 June 2010
Available online 11 June 2010

Keywords:
Ruthenium catalysis
Synthetic process
Benzothiazoles and orthanilic acids
Reaction mechanism
N-haloamines

ABSTRACT

Ruthenium–Schiff base complex catalyzed efficient protocol has been developed for the synthesis of orthanilic acids from benzothiazoles in good to excellent yields using N-haloamines. Hexa-coordinated ruthenium complex with Schiff base and triphenylphosphine ligands has been prepared and its catalytic function was invented for the synthesis of orthanilic acids. The synthetic process utilizes our efficient method for the selective and preferential oxidation of thiazole ring of benzothiazoles using N-haloamines without effecting phenyl ring. The detailed catalytic, mechanistic and kinetic investigations have been made for the synthetic reactions. Solvent isotope studies have been made in H_2O–D_2O and the reactions were carried out at different temperatures. Under the identical set of conditions, the kinetics of catalyzed reactions has been compared with uncatalyzed reactions and found that the catalyzed reactions are 9–11 folds faster. The catalytic constants (K_C) have been calculated for each N-haloamine at different temperatures and the values of activation parameters with respect to the catalyst have been evaluated. Spectroscopic evidence for the formation of 1:1 complex between N-haloamine and ruthenium has been obtained. The observed results have been explained by a plausible mechanism and the related rate law has been deduced.

1. Introduction

The synthesis of orthanilic acids is an important task due to their valuable applications in both laboratory and industry. The importance of orthanilic acids resides in their widespread uses in the syntheses of various organic dyes [1], and their potential uses as reagents for the synthesis of pharmaceutically active heterocyclic compounds. The amide and sulfamoyl derivatives of orthanilic acids with certain related substitutes have significant medicinal importance such as sulfa drugs and salidiuretic active agents [2,3]. One of the most relevant methods for the synthesis of orthanilic acids involves the reduction of *o*-nitrobenzenesulfonyl chloride or oxidation of di-*o*-nitrophenyl disulfide [4]. However, there was not much attention paid towards the synthesis of these compounds by alternative methods other than the nitro group reductions or sulfide/thiol group oxidations. Hence, we felt it would be keen interest to investigate the alternative method for the synthesis of orthanilic acids. In this regard, we have developed an easy and selective synthetic process by the oxidation of benzothiazoles at thiazole ring to produce orthanilic acids in good to excellent yields.

Synthesis of organic molecules using oxidation process plays a central role in organic chemistry both at laboratory and industrial level. Selective oxidation processes are important in synthesis of organic compounds, biomolecules and pharmaceuticals, because these reactions create new functional groups or modify existing functional groups in a molecule [5,6]. Several methods are available for the synthesis and oxidation of organic molecules using different oxidants ranging from metal oxidants to atmospheric O_2. However, still there is a need for developing environmentally friendly methodologies and introduction of safe, cost-effective and stable reagents for the synthesis of organic molecules via oxidation process. The development of new processes for the selective oxidations with environmentally friendly oxidants has potential practical applications in organic synthesis. In this regard, a large group of compounds entitled sodium N-haloarenesulfonamidates (organic haloamines) are widely used in fine organic synthesis [7]. The sodium N-haloarenesulfonamidates (Fig. 1; henceforth abbreviated as N-haloamines) are the new class of oxidants and reagents with polarizable N–X bond, which attracts the attention of chemists in recent times. These compounds are the precursors of halonium cations, hypohalite species, and N-anions capable of acting both as bases and as nucleophiles [8]. These compounds resemble hypohalites in their oxidative behaviour and, even though less familiar, they are more stable than hypohalites

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doi:10.1016/j.molcata.2010.06.006

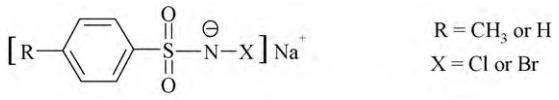
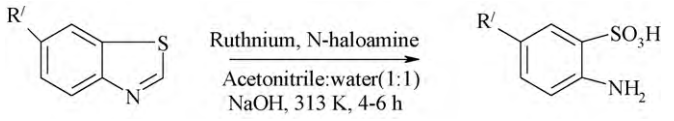


Fig. 1. Structure of N-haloamines.



Scheme 1. Ruthenium catalyzed synthesis of orthanilic acids from benzothiazoles.

[9,10]. Consequently, these reagents react with a wide range of functional groups effecting an array of molecular transformations [7,8]. The prominent members of N-haloamine class of compounds are chloramine-T (p-$CH_3C_6H_4SO_2NClNa.3H_2O$ or CAT), chloramine-B ($C_6H_5SO_2NClNa.1.5H_2O$ or CAB) and the corresponding bromine analogues bromamine-T (p-$CH_3C_6H_4SO_2NBrNa.3H_2O$ or BAT) and bromamine-B ($C_6H_5SO_2NBrNa.1.5H_2O$ or BAB). Sodium N-haloarenesulfonamidates, due to their versatile properties have proved to be valuable reagents for a variety of functional group transformations [7–13]. N-haloamines act as good oxidants and reagents both in alkaline and acidic media, and have been widely used for the oxidation and synthesis of variety of organic and biomolecules [7–13].

Ruthenium has various valences (0–8) and therefore, numerous useful catalytic reactions for organic synthesis have been explored [11–15] using ruthenium. Metal complexes of ruthenium containing nitrogen and oxygen donor ligands are found to be effective catalysts for oxidation, reduction, hydrolysis, and other organic transformations [11–15]. In the present work, we have prepared a ruthenium complex with group of three tridentate O,N,N donor ligand along with triphenyl phosphine. The ligand is abbreviated in general as L and it has three potential donor sites, viz., phenolate oxygen, azomethine nitrogen and amine nitrogen. Although many catalytic applications of ruthenium towards the oxidation and synthesis of various organic molecules have been reported [11–15], a literature survey shows there are no kinetic investigations made on the synthetic reactions of benzothiazoles particularly involving ruthenium as a homogeneous catalyst.

The wide range of applications of orthanilic acids, the usefulness of ruthenium catalyst in organic reactions and versatile properties of N-haloamines, instigate us to carryout the title reaction. By keeping above points in mind, we reported herein a new and simple method for the preparation of orthanilic acids from benzothiazoles using N-haloamines and ruthenium complex catalyst (Scheme 1). The objectives of the present study are to: (i) prepare hex-coordinated ruthenium–Schiff base complex and to explore its application as catalyst system, (ii) develop an efficient synthetic process for the facile conversion of benzothiazoles to orthanilic acids, (iii) elucidate a plausible mechanism and to deduce an appropriate rate law, (iv) ascertain the various reactive species, (v) assess the relative rates of oxidation of benzothiazoles towards N-haloamines, (vi) find the catalytic efficiency of ruthenium and to compare the reactivity with that under uncatalyzed oxidation and (vii) study the solvent isotope using D_2O. The present method developed for the synthesis of orthanilic acids from benzothiazoles offers many advantages including high conversion, short reaction times and the involvement of non-toxic reagents.

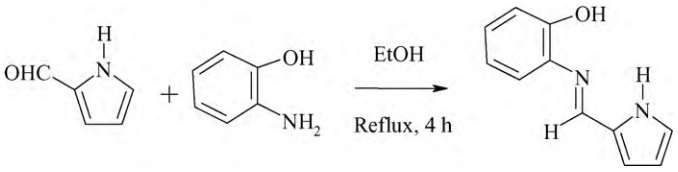
2. Experimental

2.1. Materials

Melting points were determined on X-4 apparatus and were uncorrected. IR spectra were obtained using Shimadzu FTIR-8900 spectrometer. MS data was obtained on 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. Chloramine-T (E-Merck) and chloramine-B (Fluka) were purified by the method of Morris et al. [10] and Verger and Perlin [16], respectively. Benzothiazoles (Lancaster, Sigma–Aldrich and Fuka) were acceptable grade of purity and used as received. A solution of benzothiazole by aqueous acetonitrile (1:1 water:acetonitrile) was employed for the kinetic study. Solvent isotope studies were made with D_2O (99.4%) supplied by Bhabha Atomic Research Center, Mumbai, India. Reagent grade chemicals and doubly distilled water were used throughout. Bromamine-T and bromamine-B were prepared by the literature procedures [17,18] and the solutions of these were prepared in 1:1 ratio of acetonitrile:water and standardized by iodometric procedure and preserved in brown bottles to prevent photochemical deterioration.

2.2. Preparation of catalyst

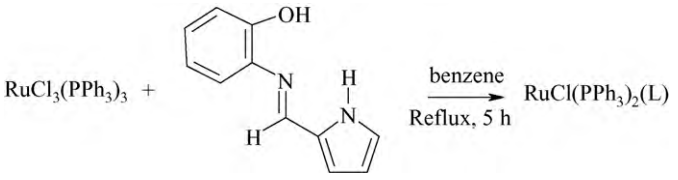
The Schiff base ligand was prepared by the reaction between pyrrole-2-aldehyde and 2-aminophenol. Ethanolic solutions of pyrrole-2-aldehyde (0.01 mol; 20 mL) and 2-aminophenol (0.01 mol; 20 mL) were mixed and refluxed for about 4 h. The reaction mixture was evaporated to a small volume and left to cool. The resulting Schiff base ligand was precipitated on cooling and then was filtered off, washed with ethanol and recrystallized from ethanol. The purity of the Schiff base ligand was monitored on TLC using eluants 1:1 ethyl acetate and petroleum ether and separated by column chromatography (yield = 90%).



(1)

The ligand was characterized by IR spectral analysis. IR spectra of Schiff base showed a strong band around 1580–1600 cm^{-1} for the free azomethine (–CH=N–) group. In the ruthenium complex, this band is shifted to the region 1522–1543 cm^{-1}, indicating the coordination of the Schiff base through the azomethine nitrogen [19]. Further the ligand was characterized by mass spectral analysis.

The starting complex $[RuCl_3(PPh_3)_3]$ was prepared according to the reported literature procedure [20]. The ruthenium complex was prepared by the reaction between $[RuCl_3(PPh_3)_3]$ and Schiff base. The mixture (1:1 ratio) of $[RuCl_3(PPh_3)_3]$ (0.1 mmol) and Schiff 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 75%.



(2)

The ruthenium complex was characterized spectroscopically as follows:

IR spectra of Schiff base showed a strong band around 1580–1600 cm^{-1} for the free azomethine (–CH=N–) group and this

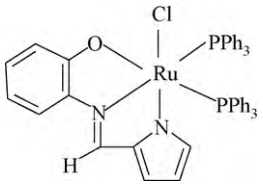


Fig. 2. Structure of $[RuCl(PPh_3)_2Cl]$.

band was shifted to the region 1522–1543 cm^{-1} in metal complex, indicating that one of the coordination is through azomethine nitrogen [19] of Schiff base. Strong band was observed in the region 1270–1300 cm^{-1} for free Schiff 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 other coordination is through phenolic oxygen atom [21]. The characteristic absorption band for secondary amine N–H stretching is observed in the region 3300–3000 cm^{-1}. But this band was absent in the complex indicating that the one more coordination site is tertiary nitrogen atom of pyrrole ring to the metal ion [22]. The other characteristic bands due to triphenylphosphine were also present in the expected region, and hence these are attributable to the coordinated N,N,O-donor ligand (L). Elemental analysis of the complex $C_{47}H_{38}N_2OP_2ClRu$ was also made and the percentage of carbon, hydrogen and nitrogen was found to be 66.5, 4.45 and 3.30 respectively.

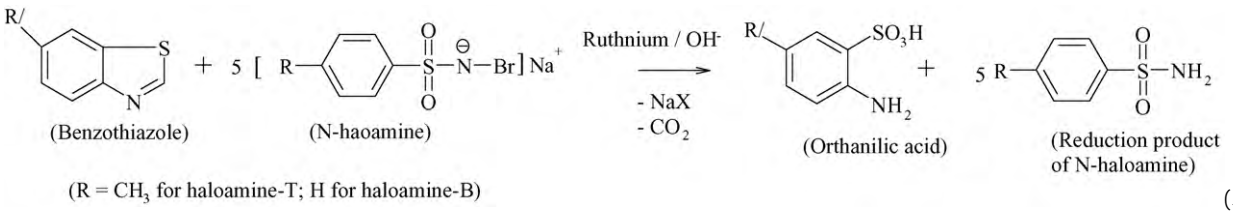
The electronic spectrum of ruthenium complex showed charge transfer bands [23]. Due to the relatively high oxidizing properties of ruthenium, the charge transfer bands of type $L_{\prod y} \rightarrow t_{2g}$ are prominent in the lower energy region. The electronic spectrum of the complex is showed in the 360 nm region.

Magnetic susceptibility measurements show that the complex $[RuCl(PPh_3)_2L]$ is diamagnetic, which corresponds to the +3 state of ruthenium (low-spin $d6$, $S = 0$). ^1H NMR spectra of the complex showed broad signal within 7.03–7.60 ppm due to the coordinated PPh_3 ligands. The signal observed at 5.82 ppm for azomethine proton for the coordinated N,N,O-donor ligand (L). The expected aromatic proton signals for the coordinated ligand have been observed within 5.5–6.6 ppm.

Based on the above spectroscopic data the complex is hexacoordinated and the ligand is coordinated to the metal centre, via pyrrole N–H and phenolic O–H protons, as a dianionic tridentate N,N,O-donor. Two triphenylphosphines and a chloride are also coordinated to the metal centre in an octahedral fashion as shown in Fig. 2.

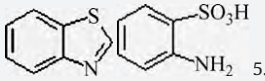
2.3. Reaction stoichiometry

Reaction mixtures containing varying ratios of N-haloamines to benzothiazole in the presence of 1.0×10^{-3} mol dm^{-2} NaOH and 1.0×10^{-6} catalyst were equilibrated at 313 K for 24 h. Determination of unreacted N-haloamine amount in reaction mixture showed that 1 mol of benzothiazole consumed 5 mol of N-haloamine, confirming the following stoichiometry:



(3)

Table 1
Ruthenium catalyzed synthesis of orthanilic acids from benzothiazoles.

Entry	Sustrate	Product	Reaction time (h min)	Yield (%)	mp (°C)
					
1			5.00	95	293 (300)
2	6-OMe	5-OMe	4.30	96	315 (314–318)
3	6-OH	5-OH	4.20	96	255 (257)
4	6-Br	5-Br	5.30	94	253 (350)
5	6-CH_3	5-CH_3	4.0	96	172 (170)
6	6-C1	5-C1	5.30	95	291 (289)
7	6-COOH	5-COOH	5.35	92	315 (320)
8	6-F	5-F	5.30	92	357 (355)
9	6-NH_2	5-NH_2	4.20	96	297 (298–300)
10	6-OAc	5-OAc	4.35	95	230 (228)
11	6-NO_2	5-NO_2	5.45	90	275 (278)
12	5-SO_3H	4-SO_3H	6.00	90	343 (340)
13	5-OH	4-OH	4.30	96	330 (328)
14	5-Br	4-Br	5.35	94	317 (318)
15	5-CH_3	4-CH_3	4.10	96	272 (275)
16	5-C1	4-C1	5.35	95	191 (189)
17	5-COOH	4-COOH	5.40	92	218 (220)
IS	5-F	4-F	5.35	92	153 (151)
19	5-NH_2	4-NH_2	4.25	96	241 (239)
20	5-OAc	4-OAc	4.40	95	190 (187)
21	5-NO_2	4-NO_2	5.50	90	247 (245

Melting points (mp) given in parenthesis refer to authetinc sample.

2.4. Procedure for the synthesis of orthanilic acids

To a stirred solution of benzothiazoles (10 mmol), bromamine-B (50 mmol) in alkaline acetonitrile/water (1:1) mixture (20 mL), catalyst (2 mmol) was added and the mixture was heated at 313 K for 4–6 h. After completion of the reaction, the reduction product of N-haloamine, *p*-toluenesulfonamide (PTS) or benzenesulfonamide (BSA) was extracted with ethyl acetate and identified by TLC and confirmed by mass spectral analysis. The aqueous part of the reaction mixture was neutralized with acid followed by solvent evaporation under reduced pressure. The residue was dissolved in dichloromethane and the dichloromethane layer was washed twice with water and then dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue thus obtained was purified by passing through a short silica gel column using dichloromethane as eluent. Evaporation of the solvent yields orthanilic acids around 95%. The products were identified by TLC and mp by comparing with authentic samples. Further, the compounds were confirmed by mass spectral analysis. The reaction times and yields are given in Table 1. Alternatively, after extracting out *p*-toluenesulfonamide, the aqueous layer was neutralized with acid and the orthanilic acids are estimated as their zinc orthanilates. The procedure for the estimation is as follows: to the reaction mixture, calculated volume of 1 mol dm^{-3} HCl was added, followed by 10 mL of pH 5.0 buffer and 10 mL of 1% zinc chloride. The precipitate formed was filtered, dried at 105–110 °C and the recovery of $(C_6H_7SO_3N)_2$ Zn was found be around 95%.

2.5. Kinetic measurements

The detailed kinetic experiments were made with respect to conversion of benzothiazole to orthanilic acid with four N-

haloamines as model reaction. The reactions were carried out under pseudo first-order conditions with a known excess of [benzothiazole]$_o$ over [N-haloamines]$_o$ at 313 K. The reactions were 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 benzothiazole, NaOH, catalyst and aqueous acetonitrile (1:1 water:acetonitrile) (to keep the total volume constant for all runs) were introduced in to the tube and thermostated at 313 K until thermal equilibrium was attained. A measured amount of N-haloamines solution, also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The progress of the reaction was monitored by the iodometric determination of unreacted N-haloamines in aliquots (5 mL each) 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 [N-haloamine] vs. time were reproducible within ±5%.

3. Results

3.1. Synthesis of anthranilic acids

Synthesis of orthanilic acids from benzothiazoles was achieved using catalytic amounts of ruthenium in acetonitrile/water (1:1) at 313 K by N-haloamines with 1:5 benzothiazoles:N-haloamines ratio in the presence of alkali. The products and the yields were summarized in Table 1. In general substrates containing electron-donating moieties found to be more reactive and required shorter reaction times compared to substrates containing electron-withdrawing groups. The synthetic process proceeds with the formation of 2-benzothiazolones and 2-aminothiophenols as the two intermediates. Benzothiazoles first utilize 1 mol of N-haloamine to form 2-2-benzothiazolones followed by the formation of 2-aminothiophenol by utilizing one more mole of N-haloamine. So formed 2-aminothiophenols consume another 3 mol of N-haloamine to yield ultimate and desired compounds, orthanilic acid. The detailed mechanism for the reactions is depicted in Scheme 3.

The reactions were studied in various solvents (acetonitrile, 1,2-dichloromethane, ethanol, and acetonitrile/water (1:1) mixture). The mixture of acetonitrile/water (1:1) was found to be the best solvent system. The reactions were found to be highly dependent upon pH of the system. To evaluate the effect of pH, the reactions were carried out under similar experimental conditions at different pH's using NaOH. At neutral pH, the oxidation reactions were found to be very slow, however the reaction rates increase with increasing in pH (addition of NaOH). This behavior of the reaction is attributed to the dissociation of N-haloamines in aqueous medium by furnishing different reactive species. This behaviour of dissociation of N-haloamines is well explained in discussion part. Due to the increase of rate in the presence of NaOH, the reactions were carried out at 1.0×10^{-2} mol dm^{-3} NaOH.

3.2. Kinetics of synthesis of orthanilic acid from benzothiazole

The kinetics of synthesis of orthanilic acid from benzothiazole by CAT, CAB, BAT, and BAB (henceforth abbreviated as N-haloamine) has been investigated at several initial concentrations of the reactants in the presence of NaOH and micro-quantity of ruthenium catalyst at 313 K. It has been observed that the similar kinetic behavior was observed with all the four N-haloamines under the identical experimental conditions.

With the benzothiazole in excess, at constant [NaOH], [ruthenium], [benzothiazole]$_o$ and temperature, plot of log [N-haloamine] vs. time is linear ($r > 0.9910$) indicating a first-order dependence of rate on [N-haloamine]$_o$. The values of pseudo first-order rate constants (k') are given in Table 2. Further, the values of k' are unaffected with variation of [N-haloamine]$_o$, confirming first-order dependence on [N-haloamine]$_o$. Under the similar experimental conditions, an increase in [benzothiazole]$_o$ led to an increase in the k' values (Table 2). Plots of log k' vs. log [benzothiazole] were linear (Fig. 3; $r > 0.9908$) with unit slopes, showing a first-order dependence of the rate on [benzothiazole]$_o$. Further, plots of k' vs. [benzothiazole] were linear ($r > 0.9980$) passing through the origin, confirming the first-order dependence on [benzothiazole]$_o$. Furthermore, the second-order rate constants $k'' = k'/$[benzothiazole]$_o$ are nearly the same for all the cases establishing a first-order dependence on the [benzothiazole]$_o$ (values are not shown).

The rate of the reaction increases with increase in [NaOH] (Table 3) and plots of log k' vs. log [NaOH] were linear (Fig. 4; $r > 0.9904$) with positive slopes (0.4–0.45), indicating fractional-order dependence of rate on [NaOH]. Further, the rate of the

Table 2
Effect of varying reactant concentrations on the reaction rate at 313 K.

10^3 [N-haloamine] (mol dm^{-3})	10^2 [Benzothiazole] (mol dm^{-3})	10^4 k' s^{-1}			
		CAT	CAB	BAT	BAB
0.5	2.0	8.61	16.4	26.2	54.6
1.0	2.0	8.80	16.7	26.8	54.2
2.0	2.0	8.50	16.5	26.6	54.5
4.0	2.0	8.70	16.3	26.5	54.8
8.0	2.0	8.30	16.2	26.4	54.2
2.0	0.5	2.11	4.12	6.45	13.8
2.0	1.0	4.31	8.31	13.3	27.8
2.0	2.0	8.50	16.5	26.6	54.5
2.0	4.0	17.1	33.2	53.1	110
2.0	8.0	34.4	67.1	107	225

[NaOH] = 1.0×10^{-2} mol dm^{-3}; [ruthenium] = 1.0×10^{-6} mol dm^{-3}.

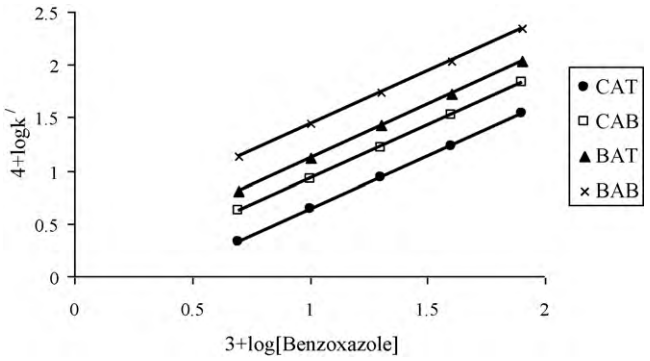


Fig. 3. Plots of log k' vs. log [benzothiazole].

Table 3
Effect of varying NaOH and ruthenium concentrations on the reaction rate at 313 K.

10^2 [NaOH] (mol dm^{-3})	10^6 [Ruthenium) (mol dm^{-3})	10^4 k' s^{-1}			
		CAT	CAB	BAT	BAB
0.25	1.0	4.47	8.62	14.1	28.5
0.5	1.0	6.75	13.2	21.2	43.2
1.0	1.0	8.50	16.5	26.6	54.4
2.0	1.0	11.6	22.5	36.6	74.6
4.0	1.0	15.5	30.5	48.8	99.3
1.0	0.25	3.03	6.00	9.45	19.4
1.0	0.5	4.85	9.65	15.2	31.1
1.0	1.0	8.50	16.5	26.6	54.4
1.0	2.0	13.4	26.5	42.4	86.0
1.0	4.0	21.5	42.6	67.9	137

[N-haloamine]$_o$ = 2.0×10^{-3} mol dm^{-3}; [benzothiazole]$_o$ = 2.0×10^{-2} mol dm^{-3}.

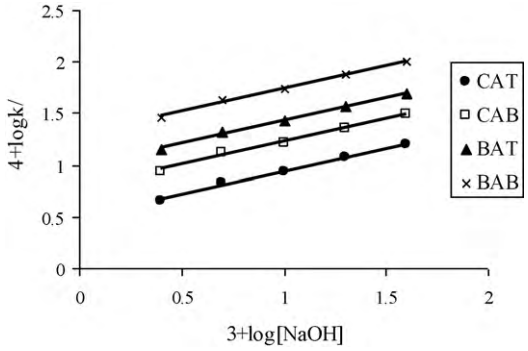


Fig. 4. Plots of log k' vs. log [NaOH].

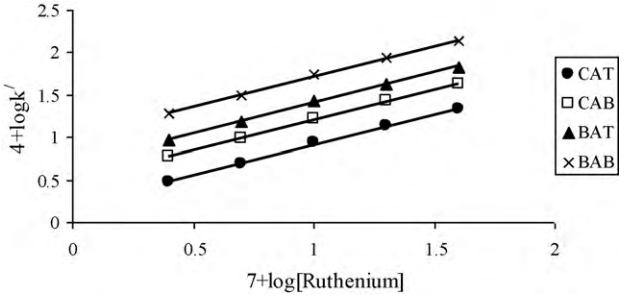


Fig. 5. Plots of log k' vs. log [catalyst].

reaction increases with increasing [ruthenium] (Table 3) and a plot of log k' vs. log [ruthenium] is linear (Fig. 5; $r > 0.9911$) with slopes less than unity (0.71) indicating a fractional-order dependence of rate on [ruthenium]. Addition of *p*-toluenesulfonamide (PTS) or benzenesulfonamide (BSA), a reduction product of N-haloamines, (1.0×10^{-3}–4×10^{-3} mol dm^{-3}), to the reaction mixture did not affect the rate significantly. This indicates that neither PTS nor BSA is involved in any step prior to the rate-limiting step in the scheme proposed.

The effect of ionic strength (I) of the medium on the rate was studied in a range of 0.10–0.50 mol dm^{-3} using $NaClO_4$ solution, keeping the other experimental conditions constant. The rate was found to be unaffected with the addition of $NaClO_4$. Rate studies were carried out in H_2O–MeOH mixtures having different compositions (0–30% (v/v)), thereby varying the dielectric constant of the solvent medium. The rate was found to decrease with increase in MeOH content (Table 4) and plots of log k' vs. $1/D$ were linear (Fig. 6; $r > 0.9901$) with negative slopes. Blank experiments performed with MeOH indicate that there was no oxidation of MeOH by any of the four N-haloamines under the selected experimental conditions.

Rate studies in D_2O medium for CAT and BAB revealed that k' (H_2O) = 8.5×10^{-4} s^{-1} and 54.4×10^{-4} s^{-1}, and k' (D_2O) = 11.9×10^{-4} s^{-1} and 75.5×10^{-4} s^{-1} respectively. The

Table 4
Effect of varying dielectric constant (D) of the medium on the rate of the reaction at 313 K.

% [MeOH] (v/v)	D	10^4 k' s^{-1}			
		CAT	CAB	BAT	BAB
0.0	76.73	8.50	16.5	26.6	54.4
10.0	72.37	7.36	15.3	23.8	50.4
20.0	67.48	6.63	13.7	21.5	44.0
30.0	62.71	5.83	11.4	18.2	37.7

[N-haloamine]$_o$ = 2.0×10^{-3} mol dm^{-3}; [benzothiazole]$_o$ = 2.0×10^{-2} mol dm^{-3}; [NaOH] = 1.0×10^{-2} mol dm^{-3}; [ruthenium] = 1.0×10^{-6} mol dm^{-3}.

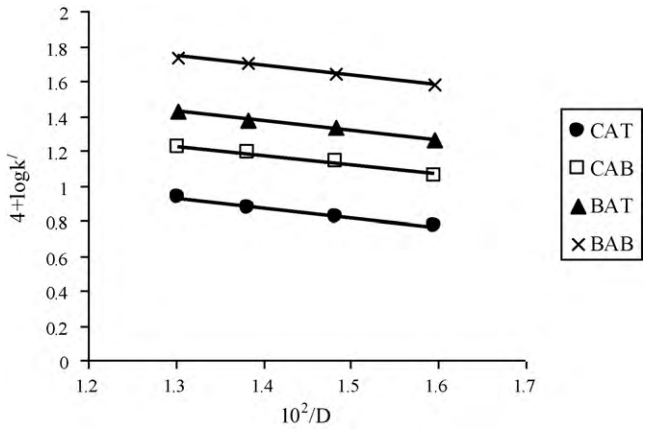


Fig. 6. Plots of log k' vs. 1/D.

Table 5
Solvent isotope studies for the synthesis of orthanilic acid by CAT and BAB in H_2O–D_2O mixtures at 313 K.

Atom fraction of deuterium (n)	k'_n s^{-1}		$(k'_o/k'_n)^{1/2}$	
	CAT	BAB	CAT	BAB
0.00	8.50	54.4	1.0	1.0
0.25	9.62	60.3	0.94	0.96
0.50	10.5	65.7	0.90	0.92
0.75	11.2	70.2	0.87	0.89
0.95	11.9	75.5	0.84	0.86

[N-haloamine]$_o$ = 2.0×10^{-3} mol dm^{-3}; [benzothiazole]$_o$ = 2.0×10^{-2} mol dm^{-3}; [NaOH] = 1.0×10^{-2} mol dm^{-3}; [ruthenium] = 1.0×10^{-6} mol dm^{-3}.

formal solvent isotope effect ratio k' (H_2O)/k' (D_2O) = 0.71 and 0.72 for these two N-haloamines. Solvent isotope studies were made using H_2O–D_2O mixtures for CAT and BAB (Table 5). The effect of the temperature on the rate was studied by performing the kinetic experiments at various temperatures (303–323 K), keeping other experimental conditions constant. From the linear Arrhenius plots of log k' vs. $1/T$ ($r > 0.9921$), the values of activation parameters (E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$) for the overall reaction were evaluated. These data are summarized in Table 6.

At experimental conditions the addition of NaCl or NaBr (1.0×10^{-3} to 4.0×10^{-3} mol dm^{-3}) did not alter the rate of the reaction. These results indicate that there is no role for halide ions in the reaction. The addition of the reaction mixtures to aqueous acrylamide monomer solutions, kept in the dark, did not initiate polymerization, confirming the absence of any free radical species

Table 6
Temperature dependence and values of composite activation parameters for the synthesis of orthanilic acid by N-haloamines in the presence and absence of ruthenium catalyst.

Temperature	10^4 k' s^{-1}			
(K)	CAT	CAB	BAT	BAB
303	2.90[a] (0.20)[b]	6.25 (0.45)	12.5 (1.00)	27.0 (2.30)
308	5.51 (0.34)	10.5 (0.92)	15.8 (1.69)	42.0 (4.00)
313	8.50 (0.80)	16.5 (1.65)	26.6 (2.65)	54.0 (5.2)
318	12.0 (1.44)	20.0 (2.45)	35.0 (4.00)	65.0 (8.0)
323	19.0 (2.10)	33.0 (4.20)	48.0 (6.10)	93.0 (12.5)
E_a (kJ mol^{-1})	71.1 (96.2)	62.8 (87.9)	52.7 (71.1)	44.7 (62.8)
$\Delta H^{\neq}$ (kJ mol^{-1})	68.5 (93.6)	60.0 (85.3)	50.0 (68.5)	42.2 (60.2)
$\Delta G^{\neq}$ (kJ mol^{-1})	79.0 (90.0)	78.5 (87.0)	78.0 (85.0)	77.0 (84.0)
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−25.2 (−1.04)	−57.5 (−4.18)	−93.5 (−15.6)	−124 (−20.9)

Values in parentheses refer in the absence of ruthenium catalyst.
[a] [N-haloamine]$_o$ = 2.0×10^{-3} mol dm^{-3}; [benzothiazole]$_o$ = 2.0×10^{-2} mol dm^{-3}; [NaOH] = 1.0×10^{-2} mol dm^{-3}; [ruthenium] = 1.0×10^{-6} mol dm^{-3}.
[b] Experimental conditions are the same as 'a' without ruthenium catalyst.

generated in the reaction sequence. The control experiments were also performed under similar reaction conditions without the N-haloamines.

4. Discussion

4.1. Reactive species of N-haloamines

Investigations of Morris et al. [10], Bishop and Jennings [9], Pryde and Soper [24] and Hardy and Johnston [25] have shown the existence of similar equilibria of N-metallo-N-arylhalosulfonamides (N-haloamines) in aqueous media. Depending on the pH, N-haloamines exhibits the different equilibria in aqueous solutions [10,9,24,25].

In alkaline solutions of N-haloamines, RNX_2 does not exists, and the possible oxidizing species are RNX^- and OX^- anions, which could be transformed into more reactive species RNHX and HOX, during the course of the reaction in alkali retarding steps. Several workers have observed the retarding effect of OH^- ions on the rate of haloamines with a number of substrates [26–28] and have suggested that the reactivity of weakly alkaline solutions of haloamines is due to the formation of the conjugate acid RNHX from RNX^- in OH^- retarding step ($RNX^- + H_2O \rightleftarrows RNHX + OH^-$). But in the present investigations, the OH^- ions increases the rate of the reaction clearly indicates RNX^- as the reactive oxidizing species ($RNHX + OH^- \rightleftarrows RNX^- + H_2O$). In earlier work [11–13], the positive influence of OH^- ion on the rate of haloamine reactions with a number of compounds have been observed and suggested RNX^- as the reactive oxidizing species. In the present investigations, the rate of the reaction is accelerated by OH^- ions clearly indicates that the anion RNX^- is the most likely reactive species of N-haloamines involved in the oxidative conversion of benzothiazoles to orthanilic acids.

4.2. Reactive species of ruthenium complex

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

$$[RuCl_3(PPh_3)_2(L)] + OH^- \rightleftarrows [Ru(OH)(PPh_3)_2(L)] + Cl^- \quad (4)$$

Hrdroxylated species of ruthenium has been postulated as the reactive species in alkaline medium for the synthesis of orthanilic acids from benzothiazoles.

4.3. Evidence showing complex formation between ruthenium and CAT

The existence of complex between ruthenium and CAT was evidenced from the UV–visible spectra of both ruthenium and ruthenium–CAT mixture, in which a shift of ruthenium from 360 to 345 nm was observed, indicating the formation of a complex.

The complex formation between metal ion ruthenium and CAT was given by the following equilibrium (Eq. (5)):

$$M + nS \overset{K}{\rightleftharpoons} (MS_n) \quad (5)$$

Here, M and MS_n are two metal species with different extinction coefficients. For the equilibrium (12), Ardon [29] has derived the following relation (Eq. (6)):

$$1/\Delta A = 1/[S]^n\{1/\Delta E[M_{Total}]K\} + 1/\Delta E[M_{Total}] \quad (6)$$

where, K is the formation constant of the complex, $[S]$ is the concentration of CAT, ΔE is the difference in extinction coefficient between two metal species, $[M]_{Total}$ is the total concentration

$$RNHX + OH^- \overset{K_1}{\rightleftharpoons} RNX^- + H_2O \quad \text{(i) fast}$$

$$RNX^- + \text{Ruthenium} \overset{K_2}{\rightleftharpoons} Y \quad \text{(ii) fast}$$

$$Y + \text{Benzothiazole} \xrightarrow{k_3} Y' \quad \text{(iii) slow and rds}$$

$$Y' + RNX^- \xrightarrow{k_4} \text{Products} \quad \text{(iv) fast}$$

Scheme 2. General mechanistic scheme for the synthesis of orthanilic acids from benzothiazoles.

of metal species and ΔA is the absorbance difference between ruthenium–CAT mixture and ruthenium alone. Eq. (6) is valid when $[S]$ is much higher than $[M]_{Total}$. According to Eq. (6), a plot of $1/\Delta A$ vs. $1/[S]$ or $1/[S]^2$ should be linear with an intercept in case of 1:1 or 1:2 type of complex formation between M and S. The ratio of intercept to slope of this linear plot gives the value of K.

Ruthenium complex in aqueous alkaline acetonitrile medium containing CAT showed an absorption peak at 345 nm (λ_{max} for the complex). The complex formation studies were made at this λ_{max} of 345 nm. In a set of experiments, the solutions were prepared by taking different amounts of CAT (0.5×10^{-3} to 8×10^{-3} mol dm^{-3}) at constant amounts of ruthenium (1.0×10^{-6} mol dm^{-3}) and NaOH (0.01 mol dm^{-3}) at 313 K. The absorbance of these solutions was measured at 345 nm. The absorbance of ruthenium in alkaline medium is also measured at same wavelength (345 nm). The difference of these absorbance (with and without CAT) gave the differential absorbance, ΔA. A plot of $1/\Delta A$ vs. $1/[CAT]$ was linear ($r = 0.9900$) with an intercept suggesting the formation of 1:1 complex between ruthenium–CAT. Further, the plot of $\log(1/\Delta A)$ vs. $\log(1/[CAT])$ was also linear ($r = 0.9871$). From the slope and intercept of the plot $1/\Delta A$ vs. $1/[CAT]$, the value of the formation constant, K, of the complex was deduced and found to be 5.21×10^2.

4.4. Reaction scheme and rate law

Based on the above discussion and the observed kinetic results, the general mechanism (Scheme 2) has been proposed for the ruthenium complex catalyzed synthesis of orthanilic acids from benzothiazoles using N-haloamines in alkaline medium. In Scheme 2, Y and Y' represent the intermediate species whose structures are shown in Scheme 3. The detailed mechanism for the ruthenium catalyzed oxidative conversion of benzothiazoles is depicted in Scheme 3. Based on Scheme 3, following rate law was derived and which is consistent with all the experimental results.

$$\text{Rate} = \frac{K_6K_7k_8[\text{N-haloamine}]_t[\text{Benzothiazole}][\text{Ruthenium}][OH^-]}{[H_2O] + K_1[OH^-] + K_1K_2[\text{Pt(IV)}][OH^-]} \quad (7)$$

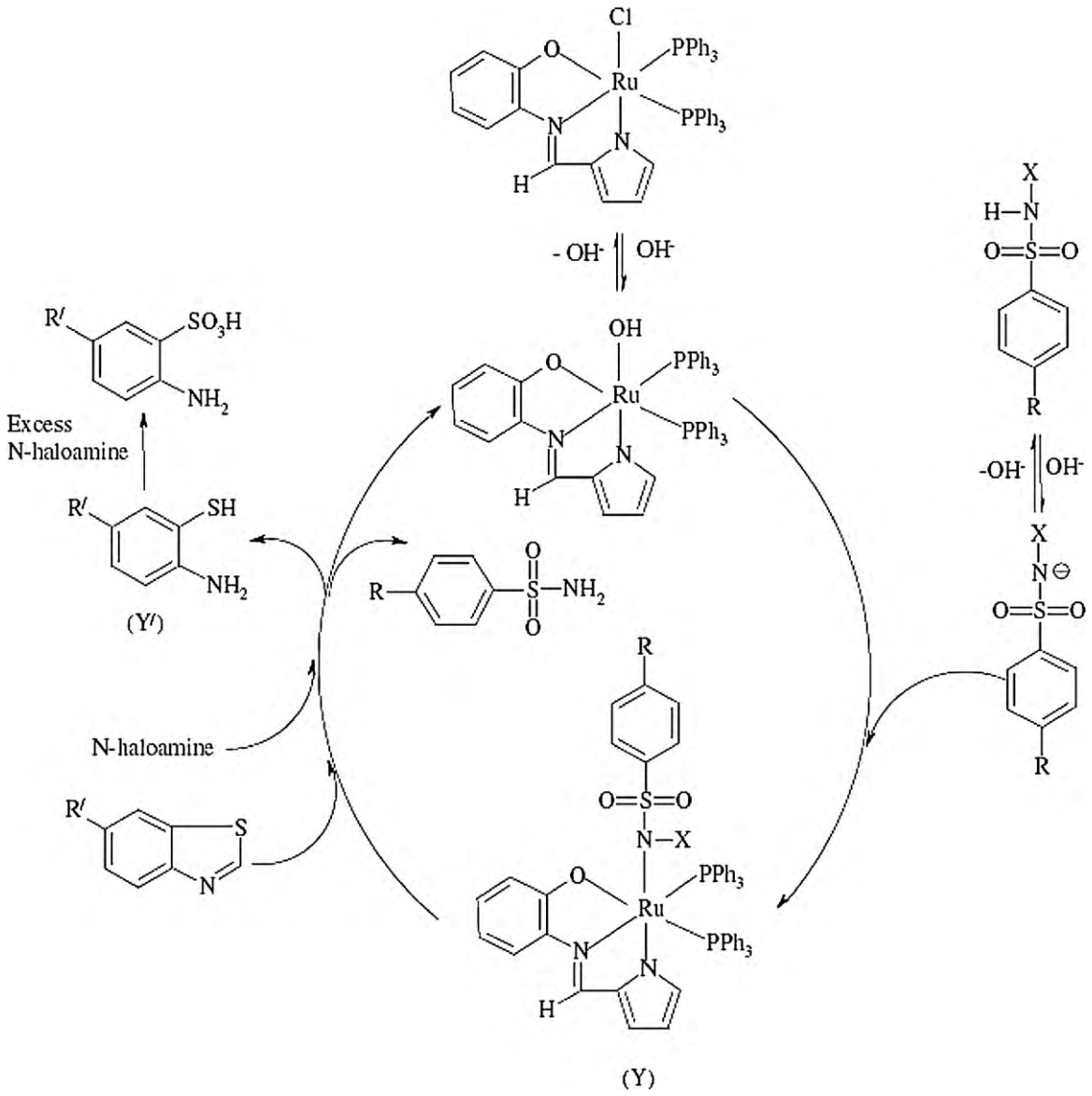
Scheme 3 and the rate law (7) are consistent with the observed experimental results and supported by the following facts:

4.5. Effect of dielectric permittivity

A decrease of reaction rate with a decrease in D (increase in MeOH content) of the medium supports the proposed mechanism. Amis and Jaffe [30] have shown that

$$\log\ k'_D = \log\ k' + Ze\mu/2.303\,kTr^2\,D \quad (8)$$

where k' is the rate constant in a medium of infinite dielectric constant and k'_D is the rate constant as function of dielectric con-



Scheme 3. Detailed mechanism for the ruthenium catalyzed synthesis of orthanilic acids.

stant 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. (18) predicts a linear relation between $\log k'$ vs. $1/D$ ($r > 0.9901$). 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. $1/D$ were linear with negative slopes ($r > 0.9901$) supporting the participation of negative ion and dipole in the rate-limiting step (Scheme 3).

4.6. Effect of solvent isotope

It is interesting to note that the rates in D_2O medium are faster than that in H_2O. Since the OD^- is a stronger base than OH^- by a factor of 2–3, the solvent isotope effect of this magnitude is expected [31]. However, the observed inverse solvent isotope effect k' (D_2O)/k' (H_2O) of 1.40 for CAT and 1.38 for BAB (Table 5) and the normal kinetic isotope effect $k'_{OH^-}/k'_{OD^-} < 1$ could counter-balance the solvent isotope effect, which can be attributed to the fractional-order dependence of rate on [OH^-]. The solvent isotope studies in H_2O–D_2O mixtures could throw light on the nature of the transition state [32,33]. The dependence of rate constant k'_n on n, the atom fraction of deuterium in a solvent mixture, is given [33] by Eq. (22):

$$k'_o/k'_n = \pi^{TS}(1 - n + n\Phi_i)/\pi^{RS}(1 - n + n\Phi_j) \quad (9)$$

where Φ_i and Φ_j are isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition state (TS) and reactant state (RS) respectively and k'_o is the rate constant in pure H_2O. If the reaction proceeds through a single transition state [33], then the Eq. (9) takes the form given in Eq. (10):

$$(k'_o/k'_n)^{1/2} = [1 + n(\Phi_j - 1)] \quad (10)$$

From Eq. (20), a plot of $(k'_o/k'_n)^1/^2$ vs. n should be linear. It is observed that such a plot is linear (Fig. 7; $r > 0.9915$) with a slope of $(\Phi_j - 1) = -0.16$ and -0.14, giving values of 0.84 and 0.86 for the fractionation factor in the cases of CAT and BAB respectively. Considering the diversity of the procedure employed, it is reasonable to assume that there is an agreement between the n values obtained. Further, a comparison with the standard plots [34] clearly implies the involvement of a single or H–D exchange during the

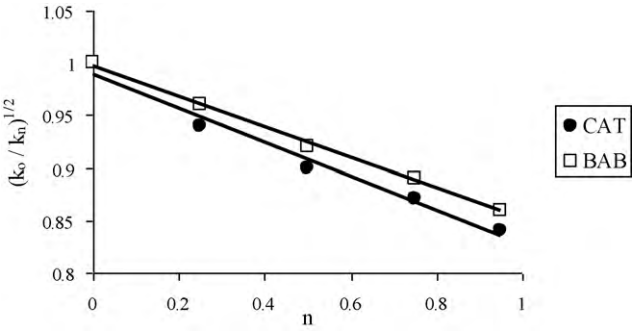


Fig. 7. Kinetc isotope studies plots.

reaction sequence. The participation of OH^- ion in the formation of transition state is thus inferred.

4.7. Activation parameters in the presence of ruthenium catalyst

The reactions were carried out at range of temperatures (303–313 K) and the energy of activations (E_a) for each reaction has been calculated from the linear Arrhenius plots of $\log k'$ vs. $1/T$ ($r > 0.9921$). The values of other activation parameters ($\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$) for the overall reaction were also evaluated. These data are summarized in Table 6. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the oxidation of benzothiazole with all the four N-haloamines are linearly related ($r = 0.9916$), with an isokinetic temperature of $\beta = 370$ K, indicating that a common mechanism operates in the synthesis of orthanilic acid of benzothiazole by all the said four N-haloamines. Further, the genuine nature of the isokinetic relationship was verified by the Exner criterion [35] by plotting $\log k'_{(303\,K)}$ vs. $\log k'_{(313\,K)}$; this plot is linear ($r = 0.9906$). The value of β was calculated from the equation $\beta = T_1(1-q)/(T_1/T_2) - q$ where q is the slope of the Exner plot and $T_2 > T_1$. The value of β was found to be 365 K. The values of β evaluated from both the plots are much higher than the temperature range used in the present work (313 K). This indicates a common enthalpy-controlled pathway for all the reactions. The high positive values of the free energy of activation and of the enthalpy of activation suggest that the transition state is highly solvated, while the high negative entropy of activation indicates the formation of rigid associated transition states. The values of $\Delta G^{\neq}$ are almost the same in the cases of all the N-haloamines, suggesting that the oxidation of benzothiazole by N-haloamines proceeds by a common mechanism.

4.8. Activation parameters in the absence of ruthenium

It was felt reasonable to compare the reactivity of these four N-haloamines towards benzothiazole in the absence of ruthenium catalyst under identical set of experimental conditions in order to evaluate the catalytic efficiency of ruthenium. The reactions were studied at different temperatures (303–323 K) in absence of Ruthenium. From the plots of $\log k'$ vs. $1/T$ ($r > 0.9902$), we evaluated the activation parameters for the uncatalyzed reactions (Table 6). The ruthenium complex catalyzed reactions were found to be 9–11 times faster and thus the observed results justify the need of a catalyst for a facile conversion of benzothiazoles by the chosen N-haloamines in alkaline medium. The catalyst ruthenium forms a complex (Y) with N-haloamines, which increases the oxidizing property of chosen N-haloamines than without ruthenium.

Table 7
Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values.

Temperature	K_C			
(K)	CAT	CAB	BAT	BAB
303	1.80	3.67	7.27	15.6
308	3.26	6.10	8.95	24.0
313	4.87	9.38	15.1	31.1
318	6.68	11.1	19.2	36.0
323	10.7	18.2	26.5	50.9
E_a (kJ mol^{-1})	68.6	62.0	54.4	44.7
$\Delta H^{\neq}$ (kJ mol^{-1})	66.0	59.0	51.8	42.0
$\Delta G^{\neq}$ (kJ mol^{-1})	67.0	66.0	64.5	63.0
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−3.89	−24.6	−41.0	−60.0

$[\text{N-haloamine}]_o = 2.0 \times 10^{-3}$ mol dm^{-3}; $[\text{benzothiazole}]_o = 2.0 \times 10^{-2}$ mol dm^{-3}; $[\text{NaOH}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[\text{ruthenium}] = 1.0 \times 10^{-6}$ mol dm^{-3}.

4.9. Catalytic activity

Moelwyn-Hughes [36] has derived the following equation relating both catalyzed and uncatalyzed reactions:

$$k_1 = k_o + K_C[\text{catalyst}]^x \quad (11)$$

in which k_1 is the observed pseudo first-order rate constant obtained in the presence of ruthenium catalyst, k_o is the pseudo first-order constant for the uncatalyzed reaction, K_C is the catalytic constant and x is the order of the reaction with respect to ruthenium. In the present investigations, 'x' values for the standard run were found to be 0.71. Then the value of K_C is calculated using the Eq. (11). The values of K_C have been evaluated for each N-haloamine at different temperatures (303–323 K) and K_C was found to vary with temperature (Table 7). Further, plots of $\log K_C$ vs. $1/T$ were linear ($r > 0.9901$) and the values of energy of activation and other activation parameters for the catalyst were computed.

4.10. Comparison of reactivity values of N-haloamines

Under identical experimental conditions, the rates are found to be higher with bromamines compared to chloramines by a factor of 3 (Table 2) and to follow the order: BAB > BAT > CAB > CAT. This is attributable to the difference in electrophilicities of the halo cations Br^+ and Cl^+ involved in the oxidation process and is also related to the ease with which these species are generated in reactions. In these reactions, the electronegativity values of Br^+ and Cl^+ play a vital role. Bromine has the electronegativity of 2.7, while chlorine has a higher value of 2.8. As the electronegativity increases, the electropositive nature decreases, since the halo cations are the reactive species in these oxidation reactions and the electropositive nature is Br > Cl. This may also be due to the moderate differences in the van der Waal's radii of the bromine and chlorine. Therefore, the reactivity of bromamines is greater than that of chloramines. This is consistent with the observed order of reactivity: BAB > BAT > CAB > CAT in the present work. Hence, it can be generalized that bromamines are stronger oxidants compared to chloramines. A similar behaviour has been reported [37,38] in the oxidation of several other substrates using N-haloamines.

Further, the observed oxidation rates are lower in BAT and in CAT compared to the rates in BAB and in CAB, the ratios k' (BAB)/k' (BAT) and k' (CAB)/k' (CAT) were found to be around 2. This indicates the participation of a $-CH_3$ group in CAT and BAT, which exerts a strong inductive effect in enriching the electron density at the polar N–X bond, thereby reducing the electrophilicity of the X atom. This explains why the reactivity of benzenesulfonamide derivatives is higher than that of toluenesulfonamide derivatives of N-haloamines. It also substantiates the observed overall reac-

tivity of BAB > BAT > CAB > CAT towards the oxidative conversion of benzothiazoles in the present work.

5. Conclusions

Ruthenium complex catalyzed synthesis of orthanilic acids was achieved efficiently using N-haloamines in the presence of alkali. Hexa-coordinated ruthenium–Schiff base complex was prepared and it has been used as the catalyst for the facile synthesis of orthanilic acids. Catalyzed synthetic reactions undergo with similar oxidation mechanism and follow the identical kinetic behaviour. Catalyzed reactions showed rates 9–11 fold faster than the uncatalyzed reactions. The present method developed for the synthesis of orthanilic acids from benzothiazoles offers many advantages including high conversion, short reaction times and the involvement of non-toxic reagents. It can be concluded that ruthenium–Schiff base complex acts as an efficient catalyst for the selective oxidative conversion of benzothiazoles to orthanilic acids by N-haloamines in alkaline medium.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.06.006.

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